

EXPERIMENTAL STUDY OF MERCURY HOMOGENEOUS REACTION CHEMISTRY UNDER POST-FLAME CONDITIONS

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Introduction

In the United States, coal combustion remains the primary anthropogenic source of mercury air pollution (1). Calculations have shown that gas phase oxidized mercury is thermodynamically favored at stack conditions, but recent studies suggest that conversion is kinetically limited (2-5). Efforts to reduce mercury emissions require knowledge of mercury speciation at stack conditions, since the oxidation state directly affects mercury capture efficiencies. Oxidized forms such as HgCl_2 , for example, are water-soluble and easily captured by wet scrubbers, whereas elemental mercury is insoluble and therefore difficult to remove.

Several recent studies have focused on developing an elementary kinetic mechanism for homogeneous Hg oxidation to predict Hg conversion in coal combustion systems. Sliger et al. (5) proposed a four step mechanism that incorporated a global reaction with Cl_2 . Widmer et al. subsequently presented an 8 step mechanism that included chlorinated species such as HOCl (6). Edwards et al. (3) expanded the Cl chemistry, Niksa and coworkers incorporated NO_x chemistry and recalculated several rate constants (4), and Qiu and co-workers further refined the rate constants and expanded the Cl chemistry (7). In each of these efforts, Cl atoms were identified as a key component in the oxidation pathway.

While the models have provided considerable insight into possible reaction pathways, detailed experimental studies of mercury oxidation in the presence of important coal combustion product gases such as SO_2 and NO in systems with the relevant radical pool are lacking. For example, Hall et al. (8) examined Hg oxidation by HCl in a heated quartz tube using bottled gas mixtures consisting of 10% O_2 in N_2 . Sliger et al. (5) used the product gases from a natural gas flame in a high quench rate system to examine Hg oxidation by HCl . Neither SO_2 nor NO were considered in this study. Similarly, Mamani-Paco and Helble (9) examined Hg oxidation by both HCl and Cl_2 in the post-flame gases produced by a methane flat flame burner. Insights into reaction pathways were gained from these studies, but there is no information provided on the importance of SO_2 and NO . Ghorishi et al. (10) conducted bench scale isothermal experiments to investigate the effects of SO_2 and H_2O and temperature on mercury oxidation in simulated flue gas mixtures, and found that no Hg oxidation by HCl occurred at temperatures below 250°C . At higher temperatures oxidation did occur, but inhibition was reported at 754°C with the addition of SO_2 . As part of an investigation that studied the effects of flue gas constituents on speciation methods, Laudal et al. (11) also examined the effects of SO_2 and NO . Results indicated that both SO_2 and NO could inhibit Hg oxidation by Cl_2 .

While these studies provide insight into inhibitory effects associated with SO_2 and NO , the relevant studies were either performed without SO_2 and NO , or with bottled gas mixtures that do not reproduce the radical pool associated with a flame environment. This study was undertaken to address these questions.

Experimental

Homogeneous oxidation of mercury was examined in a flame-fired bench-scale system shown schematically in Figure 1. Combustion gases were generated by oxidation of metered methane-oxygen-nitrogen mixtures fed to a Research Technologies Inc. multi-

element micro-diffusion flat flame burner. For these experiments, the equivalence ratio was adjusted to vary the temperature profile and the flue gas composition downstream of the flame. All experiments were conducted under either stoichiometric or fuel lean combustion conditions. A rectangular insulated stainless steel mixing chamber (0.21 m tall, 0.16 m in length and 0.17 m wide) was placed on top of the diffusion burner for gas mixing. At the back of the mixing chamber, three 6.35 mm ports were used for the injection of the mercury laden vapor stream, any chlorine containing species, and other contaminant gases (SO_2 and NO in nitrogen). Mercury vapors were generated from a mercury permeation device using nitrogen as the carrier gas. The permeation device was held in a constant temperature heating bath throughout the course of each experiment. The mercury-containing flue gas mixture then exited the mixing chamber through an outlet 0.13 m in diameter.

Gases exiting the mixing chamber flowed into a quartz reactor 80 cm long and 12.7 cm in diameter. The reactor-chamber junction was sealed with castable cement before the start of each experiment. To prevent the accumulation of condensed water as the simulated flue gases were cooled the reactor was mounted at 10 degrees to the horizontal. Heating tapes and insulation were wrapped around the reactor to provide additional heating and to reduce heat losses to the environment. Four ball and socket ports were located along the length of the reactor for sampling the reacting gas mixture.

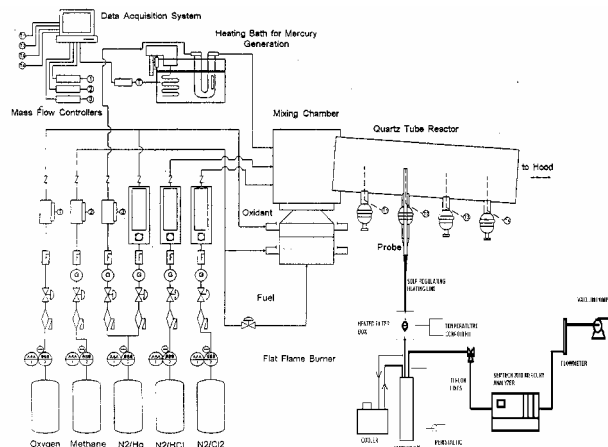


Figure 1: Schematic diagram of the mercury homogeneous oxidation experimental apparatus, modified from (9).

Quartz probes were used to collect flue gas samples from the center of the reactor. To measure the temperature at the sample ports, a thin-wire K-type thermocouple was inserted in a quartz capillary at the center of each probe.

Flue gases were sampled by a quartz probe connected to a self regulating heating line (SRHL). The SRHL core was made of TeflonTM tubing wrapped in a heating cable with a temperature controller used to maintain a tubing surface temperature of 150°C . Gas flows leaving the SRHL entered a glass fiber filter enclosed in a miniature heated filter box used to separate any particles from the gas stream. Reaction gases then entered a series of three glass impingers enclosed in a container through which water at a temperature of less than 5°C was recirculated to keep the surfaces of the impingers cold.

Gases exiting the impingers were fed to a Semtech cold vapor atomic absorption spectroscopy-based continuous Hg analyzer for analysis of Hg concentrations. Differences between oxidized and elemental mercury were determined by cycling the oxidizer (HCl or Cl₂) on and off in 30 or 60 second intervals during the course of an experiment.

The range of conditions considered in this study is presented in Table 1. In all cases, samples were extracted from sampling port 2 at a system temperature of approximately 350°C.

Table.1: Experimental test matrix used for evaluating Hg homogeneous oxidation. All concentrations in ppm.

#	Cl ₂	HCl	NO	SO ₂
1	250	0	0	0
	500	0	0	0
2	250	0	100/300	0
	500	0	100/300	0
3	250	0	0	100/400
	500	0	0	100/400
4	150	0	0	0
	250	0	0	0
5	0	100/300	0	0
6	0	100/300	100/300	0
7	0	100/300	0	100/400
8	0	300	0	0

Results and Discussion

Experiments were conducted with varying concentrations of NO, SO₂, HCl, Cl₂, and O₂ as described above and in Table 1. Typical results for an experiment involving NO and HCl addition are shown in Figure 2, and for an experiment involving SO₂ and Cl₂ in Figure 3. Error bars in each figure represent the standard deviation about the mean for a series of repeat experiments, with N ranging from 3 to 5. Addition of NO (beyond any thermal NO) is seen to have a slight inhibitory effect on Hg oxidation by HCl at HCl concentrations of 300 ppm. In contrast, SO₂ is seen to have

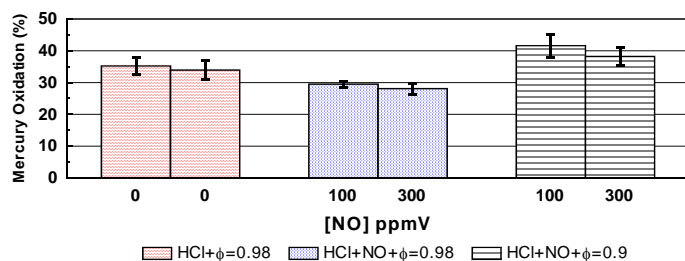


Figure 2 Hg oxidation in the presence of NO and 300 ppm HCl.

a large inhibitory effect on oxidation by Cl₂. Not shown are results from experiments with HCl and SO₂; here, very little effect was observed. In the presence of 100 ppm HCl at a flame equivalence ratio of 1, 6% of the Hg present was oxidized to HgCl₂. In the presence of 100 ppm SO₂, oxidation remained unchanged at 6%. Increasing the SO₂ concentration to 400 ppm resulted in a statistically insignificant change in Hg oxidation to 7%.

As implied by the data in Figures 2 and 3, increasing oxygen levels also contribute to an increase in Hg oxidation. Results from a series of experiments at two different flame stoichiometries in the presence of varying levels of HCl are shown in Figure 4. Differences

at low HCl concentrations are minimal but become apparent as HCl concentrations increase above 200 ppm.

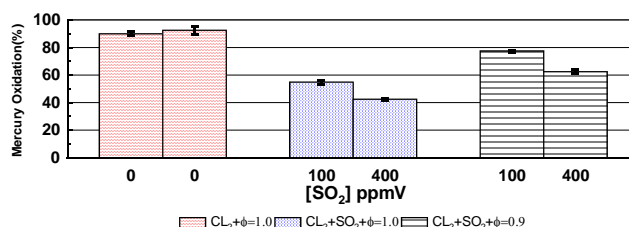


Figure 3 Hg oxidation in the presence of SO₂ and 500 ppm Cl₂.

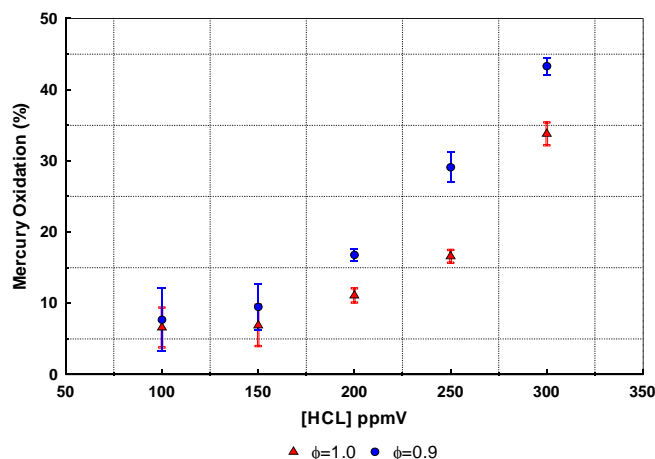


Figure 4 Hg oxidation as a function of equivalence ratio ϕ and [HCl]

Acknowledgement

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THE MECHANISTIC MODEL FOR FLUE GAS–MERCURY INTERACTIONS ON ACTIVATED CARBONS: THE OXIDATION SITE

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Introduction

Injection of fine-powdered activated carbon (AC) into the hot flue gas stream has been successful in removing a large portion of the mercury in flue gas from coal combustion, even when the mercury is mainly elemental. To minimize the amount of sorbent used, high heterogeneous reaction rates of the gas-phase elemental mercury on the carbon sorbent surface may be needed to capture the mercury in the short contact time demanded when the sorbent is quickly removed from the gas stream, such as with electrostatic precipitation of ash and carbon particulates. Part of our work has focused elucidating the nature of the interactions between the mercury and the flue gas components on AC surfaces, particularly the ACs derived from Texas (Norit FGD) and from Fort Union lignites (prepared at the Energy & Environmental Research Center [EERC]). This understanding is crucial to developing a model for mercury chemisorption and subsequent design of carbons with faster kinetics and greater capacities.

AC is an effective chemisorbent for mercury in combustion flue gas. Initial studies included a large factorial series of tests using powdered ACs that were conducted in a bench-scale system consisting of a thin fixed-bed reactor in gas streams (100° to 150°C) containing 11 to 15 $\mu\text{g}/\text{m}^3$ of Hg^0 in various simulated flue gas compositions consisting of acidic SO_2 , NO_2 , and HCl gases plus a base mixture of N_2 , O_2 , NO , CO_2 , and H_2O (1, 2). The results of these experiments showed that NO_2 or HCl-O_2 is required for effective Hg^0 capacity, no breakthrough occurred when SO_2 was omitted, and increasing SO_2 concentration gave shorter breakthrough times. H_2O is also required for breakthrough to occur. Increasing NO_2 concentration gave shorter breakthrough times. The Hg emitted after breakthrough is mostly oxidized and can exceed inlet Hg concentration. Related work showed that Hg emitted after breakthrough in the absence of HCl was $\text{Hg}(\text{NO}_3)_2$ (3). Thus the chemisorption of Hg is seriously affected by flue gas component concentrations, especially SO_2 .

Based on these capacity data, an initial model was presented (4) that described the chemisorption events following adsorption of Hg^0 . Oxidation of Hg^0 to form a bound $\text{Hg}(\text{II})$ species occurs with the electrons donated to the carbon and eventually to NO_2 or O_2 . But following oxidation, the binding site for $\text{Hg}(\text{II})$ must be basic in nature, since the $\text{Hg}(\text{II})$ is a Lewis acid. At breakthrough, the basic binding sites are completely occupied by acidic species derived from the flue gas, especially those derived from SO_2 , and then $\text{Hg}(\text{II})$ salts are displaced from the binding sites. As breakthrough occurs, the oxidation reaction decouples from the binding reaction(s), since nearly 100% oxidation occurs even after complete breakthrough, when the binding sites are completely occupied. This fact argues against any explanation for loss of capacity based on pore plugging by species resulting from acid gases, since this would inhibit both reactions. The $\text{Hg}(\text{II})$ species that forms or is released after breakthrough is volatilized as HgCl_2 or $\text{Hg}(\text{NO}_3)_2$.

The nature of the mercury–flue gas–sorbent interactions was further elucidated in x-ray photoelectron spectroscopy (XPS) experiments performed with two AC sorbents, Norit FGD and the EERC lignite-derived AC, exposed to various simulated flue gas

compositions containing Hg^0 with various levels of SO_2 , NO_2 , HCl , and H_2O for time periods before and after breakthrough of mercury (5). Because of the interference caused by silicon, XPS data could not be obtained for the mercury species present in the exposed sorbents. These studies verified that sulfur(VI) (sulfate, bisulfate, sulfonate, or sulfuric acid) is the major sulfur species on all the exposed sorbent samples, and the longer the exposure to SO_2 , the more sulfate is found in the sample. When NO_2 or H_2O was omitted from the flue gas, less sulfate was accumulated.

Thus adsorbed SO_2 is clearly oxidized on the sorbent surface to sulfur(VI) species in a process facilitated by NO_2 and H_2O , and the sulfur(VI) is the main poison for the basic sites. The XPS data also indicate that two types of chlorine are present: ionic and covalent, and that both chlorine forms disappeared from the sample at breakthrough. That chlorine is present as both chloride ion and covalent (organic) chlorine indicates that the HCl in the flue gas can donate a hydrogen ion to a basic site as well as add both hydrogen and chlorine to a basic site to form the organochlorine product. The accumulation of chlorine in the absence of SO_2 as well as the disappearance of chlorine after continued exposure in SO_2 is explained by competition of HCl with bisulfate or sulfuric acid. As more bisulfate is generated from SO_2 at the carbon surface, it displaces the HCl , owing to the high volatility of HCl .

Refined Model for the $\text{Hg}(\text{II})$ Binding Site

A refinement of the binding site model was proposed (6) that offers more detail on the nature of the carbon site and its interaction with flue gases and Hg (Figure 1). This model uses the concept of zigzag carbene structures recently proposed for states at the edges of the carbon graphene layers (7) rather than oxygen functional groups suggested by other authors. In the carbene model, the zigzag carbon atom positioned between aromatic rings is hypothesized to be the Lewis base site. The zigzag Lewis basic carbene reacts with the $\text{Hg}(\text{II})$ species as shown in Figure 1 to form an organomercury carbenium ion and also with HCl , H_2SO_4 , and SO_2 to form carbenium ions with associated chloride and sulfate, that can combine to form the observed organochlorine and possibly also ester moieties. Sulfinate functionality could also form from SO_2 .

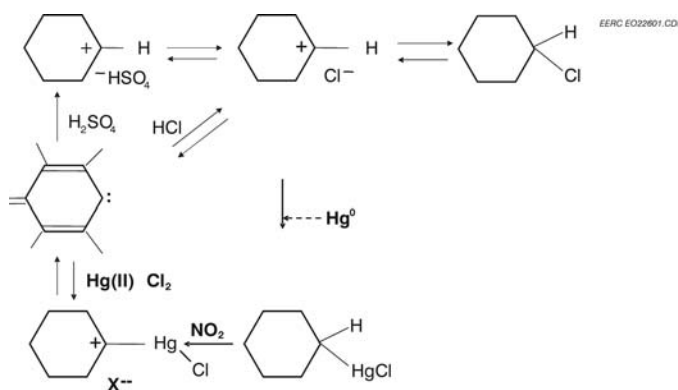


Figure 1. Oxidation mechanism – carbenium ion oxidant.

The Role of HCl

In tests conducted at relatively high HCl concentrations (50 ppm), the capture of mercury at the start was always very high (less than 5% of inlet concentration), but in very low HCl concentrations such as those obtained when low- Cl coals are burned (1 ppm), an initial breakthrough was observed at about 50%–60% of

inlet (8), followed by an increase in capture efficiency to the 5%–10% level. The higher HCl concentration thus eliminated this induction period where poor capture is obtained. It is clear that HCl is not an oxidizing reagent, since it is already in the most reduced state. This is, therefore, a promotional effect of the HCl on the activity of the carbon in catalyzing the oxidation of mercury. A similar promotional effect of adding aqueous HCl to the sorbent was reported recently by Ghorishi et al. (9).

Oxidation Site Models and Tests

The previously described carbene model for the acid gas interactions, while consistent with the breakthrough capacity and spectroscopic data, also secures the foundation for the Hg^0 oxidation reaction(s). A variation of this scheme, as shown in Figure 1, explains the promotional effect of HCl. In this oxidation mechanism, the carbenium ion intermediate, formed when protonic acids add to the carbene exactly as described above is actually the oxidation site for the adsorbed Hg^0 . Donation of electrons from the Hg^0 to the carbene forms an organomercury species. A subsequent oxidation step with NO_2 or O_2 will generate the organomercury carbenium ion. Thus HCl or other protonic acids promote the oxidation step by generating the positive carbenium ion oxidation sites, but the reaction site eventually becomes cluttered with sulfuric acid molecules. Thus at breakthrough, there are still carbenium ions for oxidation of Hg^0 , but the reaction is driven toward loss of the more volatile species, mercury and HCl.

An alternative mechanism involving the same carbene site is depicted in Figure 2. In this model, a radical carbon chlorine pair is formed either from a radical addition of HCl to a triplet state of the carbene or by homolytic cleavage of the organochlorine intermediate. The chlorine atom could oxidize the Hg^0 to form Hg(I)Cl that could combine with the carbon edge radical to form the organomercury species identical to that formed via carbenium addition. It should be noted, however, that Hg oxidation occurs perfectly well without HCl, once the sorbent is active.

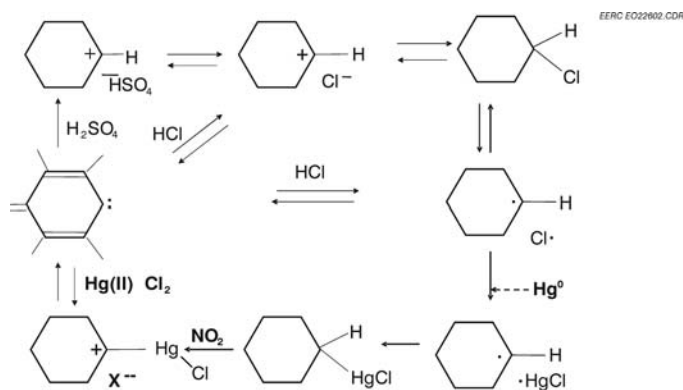


Figure 2. Oxidation mechanism – chlorine atom oxidant.

An experiment was performed to test the hypothesis that chlorine atoms are generated on the carbon surface and are responsible for the accelerated oxidation. An FGD carbon sorbent was pretreated with HCl and then with radical scavengers which should reduce reactivity. The mercury capture results showed that this sorbent oxidized Hg^0 equally as well as a sorbent untreated with radical scavenger.

Conclusions

The refinement of the mechanistic model for Hg^0 oxidation and binding is now proposed that offers more detail on the nature of the

carbon site and its interaction with flue gases and Hg. This model uses a zigzag carbene edge structure model to explain how the carbon graphene surface can provide a basic site for which acid gas components compete and how a reactive oxidation site is generated as a result of the acid addition. An alternative mechanism for oxidation involving generation of a chlorine radical was not consistent with the result from addition of a radical scavenger that would have depleted the chlorine atoms.

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PILOT-SCALE EVALUATION OF ACTIVATED CARBON-BASED MERCURY CONTROL OPTIONS FOR UTILITIES BURNING LIGNITE COAL

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Abstract

Activated carbon sorbents were evaluated for mercury removal potential in bench- and pilot-scale systems at the Energy & Environmental Research Center (EERC). The Ontario Hydro method and continuous mercury monitors were used to measure mercury species concentrations across the control technology devices with and without sorbent injection. Primarily elemental mercury (Hg^0) was measured when lignite coals from the Poplar River Plant and Freedom Mine were combusted. The effects of sorbent injection rate, particle size, and gas temperature on mercury removal were evaluated for four particulate control device options. Increasing injection rates, decreasing gas temperatures, and improving contact between the sorbent and flue gas all generally promoted mercury capture. Relative to eastern bituminous coal combustion flue gases, higher sorbent injection rates were generally required to effectively remove mercury from the lignite coal combustion flue gases. Similar issues of high Hg^0 and slow kinetics apply to other western coals as well. This paper summarizes the effects of chlorine and other additives on the oxidation and removal of mercury from flue gas.

Introduction

In general, lignite coals contain comparable levels of mercury but significantly lower levels of chlorine compared to bituminous coals. Lignite coals are also distinguished by their much higher calcium contents. These compositional differences have important effects on the quantity and form of mercury emitted from a boiler and the effectiveness of different control technologies to remove mercury from flue gas. The high chlorine content (>200 ppm) that is characteristic of many bituminous coals increases the fraction of the more easily removable mercuric compounds (Hg^{2+}), most likely mercuric chloride (HgCl_2), in the total mercury emission. Conversely, experimental results and information collection request data indicate that low-chlorine (<200 ppm) coal combustion flue gases contain predominantly Hg^0 , which is substantially more difficult to remove than Hg^{2+} .¹ Additionally, the generally high calcium contents of lignite coals may further reduce the oxidizing effect of the already low chlorine content by reactively scavenging chlorine species (Cl , HCl , and Cl_2) from the combustion flue gas.²

The most commonly considered strategy for removing mercury from coal combustion flue gas streams is the adsorption of mercury species by a solid sorbent injected upstream of a particulate control device such as a fabric filter (FF) or electrostatic precipitator (ESP). Many potential mercury sorbents have been evaluated.³ These evaluations have demonstrated that the flue gas composition and the chemical speciation of mercury affect mercury capture and its ultimate environmental fate.

Currently, powdered activated carbon (PAC) injection appears to be the most mature and promising technology available for mercury control. Research and test data suggest that activated carbons can effectively sorb both Hg^0 and Hg^{2+} . However, much of the research to date has been performed in fixed-bed reactors that simulate relatively long residence time (minutes or hours) and intimate gas-solids contact on a FF cake.⁴⁻⁹ It is equally important to investigate short residence time (seconds) in-flight capture of Hg^0

because most of the coal-burning boilers in the United States and Canada use cold-side ESPs for controlling particulate matter emissions. The projected annual cost for activated carbon adsorption of mercury in a duct injection system is significant. Carbon-to-mercury weight ratios of 3000B18,000 (gram of carbon injected per gram of mercury in flue gas) have been estimated to achieve 90% mercury removal from a coal combustion flue gas containing $10 \mu\text{g}/\text{Nm}^3$ of mercury.³ Pilot data from this project suggest that, for lignite-fired plants, the carbon-to-mercury weight ratio required may be toward the upper end of this range. More efficient carbon-based sorbents and contacting systems are required to enable lower carbon-to-mercury weight ratios to be used, thus reducing the operating costs of PAC injection.

Researchers at the Energy & Environmental Research Center (EERC) and elsewhere are striving to attain a more thorough understanding of mercury species reactions on activated carbon surfaces in order to produce more efficient sorbents.^{10,11} The removal of mercury from flue gas by activated carbon probably occurs through reactions with surface functional groups. Mercury-reactive surface functional groups may include acidic carboxyl, lactone, hydroxyl, and carbonyl or alkaline pyrone and chromene functionalities.¹⁰⁻¹⁵ The potential role of acidic and alkaline surface functional groups on mercury capture is unknown and needs to be investigated. Functional groups containing inorganic elements such as chlorine or sulfur are also possibilities.^{10,11,16-20} Although chlorine- and sulfur-bearing surface functional groups are not well characterized, the beneficial role of chlorine and the often negative impact of SO_2 and SO_3 in capturing mercury species on activated carbons are well established.^{15,21}

The EERC recently completed the first phase of a 3-year, two-phase consortium project to develop and demonstrate mercury control technologies for utilities burning lignite coal. Phase I objectives were to develop a better understanding of mercury interactions with flue gas constituents, test a range of sorbent-based technologies targeted at removing mercury dominated by the elemental form (Hg^0) from flue gases, and demonstrate the effectiveness of the most promising technologies at the pilot scale. The Phase II objective is to demonstrate and quantify sorbent technology effectiveness, performance, and cost at a sponsor-owned and/or operated power plant. This paper documents the Phase I results and provides a brief overview of the Phase II plans.

Results and Discussion

Bench-Scale Testing. Fixed-bed tests were completed on a NORIT FGD sorbent and a calcium-based sorbent. Two simulated coal combustion flue gas compositions were used during the tests as presented in Table 1. The simulated lignite flue gas composition is based on flue gas measurements made at a lignite-fired power plant and derived from the relatively low chlorine contents of the Luscar (18.0 ppmw), Beulah-Zap (12.6 ppmw), and Center (14.3 ppmw) coals. The second simulated flue gas composition in Table 1 had been used in previous testing, thus enabling comparisons to be made with other sorbent test results. The baseline flue gas contains much higher SO_2 , NO, NO_2 , and HCl concentrations but lower H_2O concentrations relative to the lignite flue gas. Test results are presented in Figures 1-3. These figures show the temporal changes in total mercury concentration downstream from the fixed-sorbent beds expressed as a percentage of Hg^0 input (nominally $10 \mu\text{g}/\text{m}^3$) into the system. Figure 1 shows results for the activated carbons prepared at the baseline conditions, unactivated chars, and a calcium-based sorbent tested in the simulated lignite flue gas (Table 1). Mercury was initially passed through the activated carbons and then effectively captured for about 3 hr. After 3 hr, mercury began to

break through the fixed-sorbent beds at progressively higher levels and was released primarily as Hg^{2+} (>90%).

Table 1. Simulated Coal Combustion Flue Gas Compositions

Component	Component, unit	Lignite	Baseline
O ₂	vol%	6	6
CO ₂	vol%	12	12
H ₂ O	vol%	15	8
SO ₂	ppmv	580	1600
NO	ppmv	120	400
NO ₂	ppmv	6	20
HCl	ppmv	1	50
N ₂		Balance	Balance

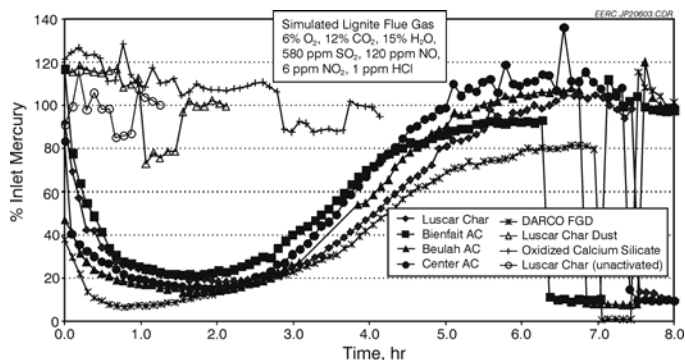


Figure 1. Bench-scale fixed-bed results under simulated lignite flue gas for carbons prepared at baseline conditions.

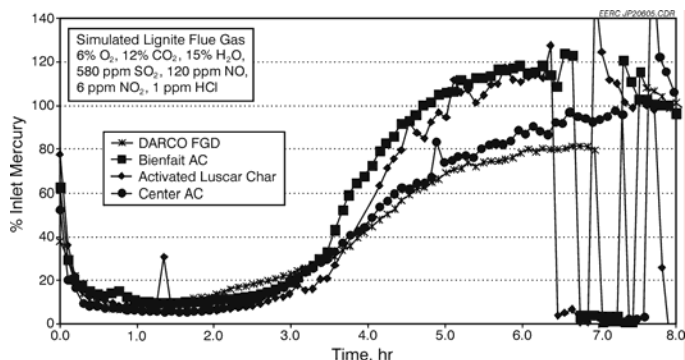


Figure 2. Bench-scale fixed-bed results under simulated lignite flue gas for carbons prepared at an increased temperature.

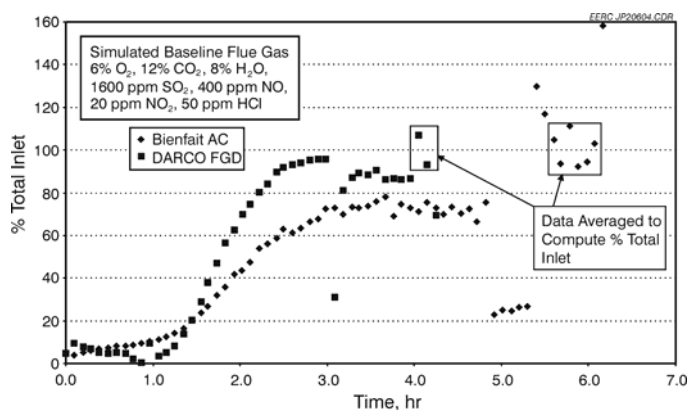


Figure 3. Bench-scale fixed-bed results under simulated baseline flue gas for Luscar coal activated at an increased temperature and NORIT FGD.

The initial breakthrough of mercury during the first 30 to 40 min of testing does not generally occur in flue gases containing higher acid gas concentrations. The unactivated sorbents and calcium-based sorbent were ineffective in capturing mercury; consequently, the tests were discontinued after 2 to 4 hr. Figure 2 compares test results for the carbons activated at an increased temperature and commercial carbon using the simulated lignite flue gas composition. Relative to the carbons activated at baseline conditions (Figure 1), results in Figure 2 indicate improved mercury capture and greater conversions of Hg^0 to Hg^{2+} (>95%). In addition, the initial breakthrough of mercury was not as significant. In order to compare results with a dataset of past test results, the Luscar coal carbon activated at an increased temperature and the NORIT FGD carbon were tested using the baseline flue gas composition in Table 1. Figure 3 test results show better initial mercury capture with no breakthrough. After 1.5 hr, the Luscar coal activated carbon showed less breakthrough compared to the NORIT FGD.

Pilot-Scale Combustor. A 580-MJ/hr (550,000-Btu/hr) pulverized coal-fired unit was used to evaluate mercury sorbent effectiveness in flue gases produced from combustion of lignite coal. The unit, shown schematically in Figure 4, is designed to generate fly ash and flue gas representative of that produced in a full-scale utility boiler. The combustor is oriented vertically to minimize wall deposits. A refractory lining helps to ensure adequate flame temperature for complete combustion. Based on the superficial gas velocity, the mean residence time of a particle in the combustor is approximately 3 seconds. The coal nozzle fires axially upward from the bottom of the combustor, and secondary air is introduced concentrically to the primary air with turbulent mixing. Coal is introduced to the primary air stream via a screw feeder and eductor. An electric air preheater is used for precise control of the combustion air temperature.

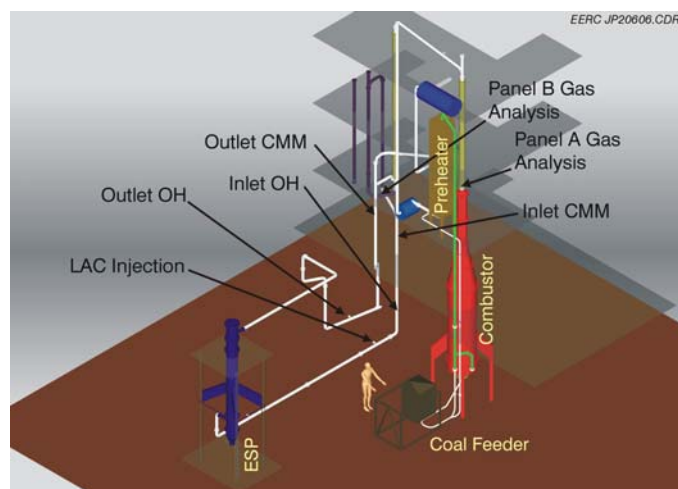


Figure 4. Schematic of the 580-MJ/hr (550,000-Btu/hr) combustion system.

The following particulate control devices were evaluated on the pilot-scale combustor as potential mercury control options: ESP, FF, combined ESPBFF, and *Advanced Hybrid*TM filter technology. Instrumentation enables system temperatures, pressures, flow rates, flue gas constituent concentrations, and particulate control device operating data to be monitored continuously and recorded on a data logger.

Pilot-Scale Tests. The activated (800°C, 1472°F) Luscar char (Bienfait) and DARCO FGD were selected for additional testing in the 580-MJ/hr (550,000-Btu/hr) pulverized coal-fired unit based on sorbent-screening results (reactivity and capacity), physical properties (particle size and surface area), cost, and consensus among project sponsors. The following variables that could potentially affect mercury emission control were tested: lignite coal source (Poplar River or Freedom Mine), control device type (ESP, FF, ESPBFF, or *Advanced Hybrid*TM filter), FF type (Gore-Tex[®] or Ryton[®]), sorbent type (steam-activated [800°C, 1472°F] Luscar char or DARCO FGD), particle size (approximate median volume diameters [MVDs] of 20 or 5 µm), sorbent injection rate, and flue gas temperature in the pollution control device. Additional tests were performed to evaluate the effectiveness of chlorine-based additives for enhancing mercury oxidation and removal.

Mercury Speciation. Figure 5 compares the average mercury species distributions, as determined by American Society for Testing and Materials Method D6784-02 (Ontario Hydro [OH]), for the Poplar River and Freedom coal combustion flue gases. The Poplar River coal combustion flue gas contains a higher total mercury concentration; however, the relative proportions of Hg⁰, Hg²⁺, and Hg(p) in both flue gases were very similar at approximately 85%, 15%, and <1%, respectively.

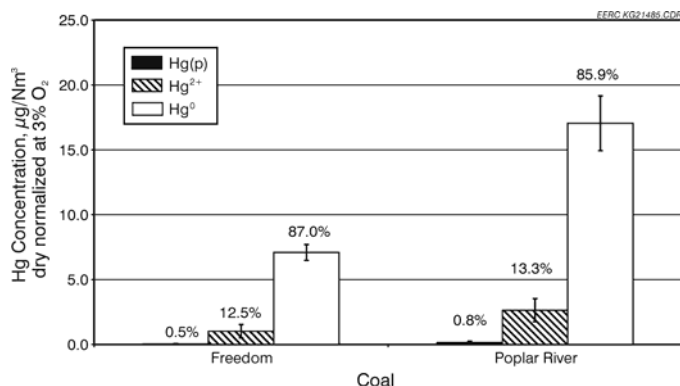


Figure 5. Comparison of average Poplar River and Freedom coal combustion flue gas (149°C, 300°F) mercury speciation results obtained using the OH method.

Effect of Varying Injection Rate on Technology Options.

Figures 6 and 7 summarize the impact of varying injection rate for the four particulate technology configurations and the Poplar River and Freedom coals, respectively. For comparison purposes, mercury removal efficiencies for each technology configuration are summarized in Table 2 using the lowest injection rate observed from either coal. In general, the Hg removal efficiencies increased with the carbon injection rate for different particulate control configurations. Clearly, the TOXECONTM configuration (injection downstream of an ESP and upstream of a FF) results in the highest reduction while using the least amount of PAC. However, in batch injection mode, the *Advanced Hybrid*TM filter provides similar performance.

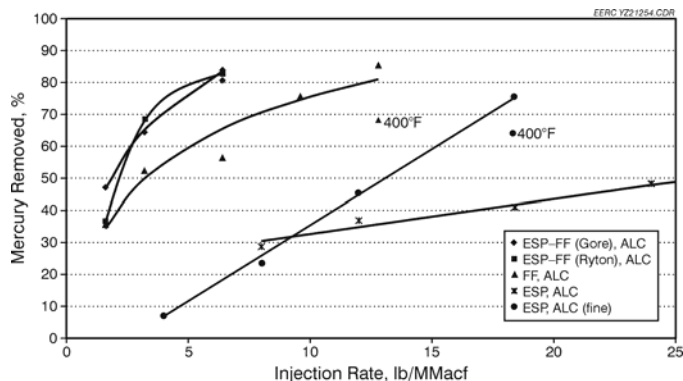


Figure 6. Particulate matter control device efficiencies for removing mercury from 149°C (300°F) Poplar River coal combustion flue gas as a function of activated (800°C, 1472°F) Luscar char injection rate.

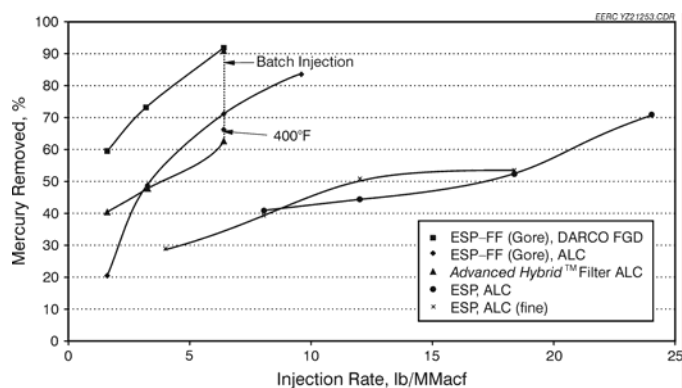


Figure 7. Particulate matter control device efficiencies for removing mercury from 149°C (300°F) Freedom coal combustion flue gas as functions of activated (800°C, 1472°F) Luscar char and DARCO FGD injection rates.

Table 2. Injection Rate (lb/MMacf)* for Target Removal Rates

Technology Configuration	50%	70%	80%
ESP Only	11.2	17.1	NA
FF Only	3.2	7.8	12.3
ESP-FF	1.9	2.92	4.4
Advanced Hybrid™ Filter	6.0	NA	6.4**

* Lowest observed rate.

** Batch injection at greater than 80% removal.

Effect of Coal. Pilot-scale data showed a higher PAC rate requirement than would be expected based on past results with other coals. Figure 8 compares the mercury removal effectiveness of PAC injection combined with pilot-scale ESP and ESPBFF devices to that obtained by Bustard and others²² with PAC injection between an ESP-FF (TOXECON™) or ESP installed on full-scale utility boilers. Coal type (i.e., composition) is an important parameter that affects the mercury removal efficiency of a control device. During the pilot-scale lignite tests with TOXECON™ and utility-scale eastern bituminous coal tests, mercury removal efficiency increased with increasing PAC injection rates. Conversely, mercury removal efficiency was never greater than 70%, regardless of the PAC injection rate into the Powder River Basin (PRB) subbituminous coal combustion flue gas. This limitation is probably caused by the low level of chlorine species that can promote mercury-activated carbon adsorption. In addition, the generally abundant lime (CaO) component of PRB subbituminous coal fly ashes reactively scavenges chlorine species (Cl, HCl, and Cl₂) from the flue gas to form CaCl₂. Figure 6 indicates that PAC injection combined with the particulate control devices installed on the full-scale boilers generally provided better mercury removal efficiency at a given injection rate relative to PAC injection followed by the pilot-scale ESP. Mercury removal efficiencies for the TOXECON™ configuration shown in Figure 6 are those observed for an eastern bituminous flue gas.

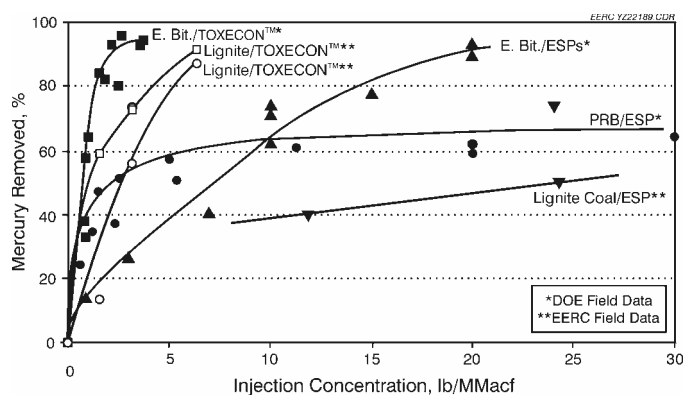


Figure 8. Pilot- and full-scale ESP and TOXECON™ mercury removal efficiencies as a function of PAC injection rate.

Effect of Chlorine. The use of chlorine and carbon-based sorbents for mercury removal has been effective in municipal, hazardous, and hospital waste incineration flue gases. Additionally, chemical kinetic modeling of bench-scale test results indicates that the introduction of HCl or NaCl into the high-temperature furnace region is likely to result in the production of atomic chlorine (Cl) and/or molecular chlorine (Cl₂), which are generally thought to be the dominant Hg⁰ reactants in coal combustion flue gases.^{23–28} Pilot-scale tests were conducted on two coals to determine if chlorine addition could improve DARCO FGD sorbent reactivity and mercury removal effectiveness from combustion flue gas. Tests were conducted on flue gases from Poplar River and Freedom coals using gaseous HCl and NaCl, respectively. Additional additives were also successfully tested and will be presented in the future.

The first round of testing was conducted on Poplar River coal, using HCl to promote sorbent reactivity. Before tests were conducted with HCl addition, the mercury concentration was measured at the outlet to evaluate the effectiveness of the DARCO FGD sorbent on mercury removal. The mercury concentration dropped from a baseline of approximately 23 µg/Nm³, prior to sorbent injection, to 5 µg/Nm³ with increasing sorbent injection rates up to 20 g/hr. At this injection rate, HCl was added at two locations under two separate tests, within the combustion zone and upstream of the ESP and carbon injection location. The flue gas temperature at the first location was approximately 930°C (1700°F) and at the second approximately 149°C (300°F), respectively. The addition of HCl at both locations did not appear to enhance sorbent reactivity and did not significantly improve the mercury removal effectiveness of the tested sorbents. More testing is needed before final conclusions can be drawn.

Additional testing was conducted on Freedom coal combustion flue gas using NaCl for sorbent enhancement. The impacts of NaCl addition with DARCO FGD were evaluated for three different particulate removal technologies: TOXECON™, Advanced Hybrid™ filter, and ESP. At baseline conditions, with no sorbent addition, mercury concentrations averaged 10 µg/Nm³, as illustrated in Figure 9. The addition of sorbent at 20 g/hr resulted in TOXECON™ mercury removal of nearly 72%. The addition of NaCl to the coal feed resulted in an additional 2 µg/Nm³ and is clearly illustrated in Figure 7. Similar trends were observed with both the Advanced Hybrid™ filter and ESP particulate control technologies.

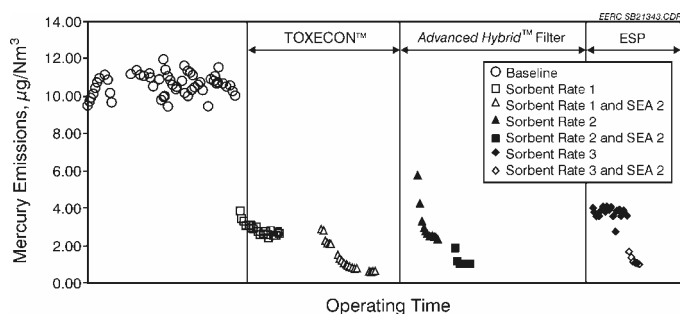


Figure 9. Impact of chlorine addition on mercury removal performance.

The preliminary results from these pilot-scale tests indicate that chlorine additives could be used to enhance mercury removal effectiveness of DARCO FGD, thereby reducing the amount of sorbent needed to achieve removal targets. Further, results suggest that the addition of NaCl to the coal would be more effective in enhancing mercury capture than HCl injection at the furnace outlet; however, differences in the test parameters (i.e., coal type, initial mercury concentration) make direct comparison of HCl and NaCl effectiveness difficult.

Using a chlorine additive has shown the potential to cut carbon rates by more than 50% for a given removal rate by using the additive at a rate below that of the carbon. Current costs for these additives range from \$35 to \$290/ton, depending on the additive. These values compare to current PAC costs of \$1000/ton. Therefore, the \$35/ton sorbent enhancement additive (SEA) has the potential to provide greater than 45% reduction in reagent costs (additive + PAC) for Hg control in systems where existing particulate control devices are used. Field testing is needed to better define performance, economics, and balance of plant impacts.

Effects of Temperature, Sorbent Size, Bag Material, and Air-to-Cloth Ratio. The impacts of temperature, sorbent size, filter material type, and air-to-cloth ratio were all presented previously and are summarized here for completeness. Temperature is a very important parameter for effective capture of mercury by PAC. Limited tests were conducted to evaluate temperature effects on sorbent performance in different configurations: ESP only, FF only, and ESP–FF. The flue gas temperature was raised from 149° to 204°C (300° to 400°F). Experimental data in Figures 6 and 7 and data presented previously show that mercury removal efficiencies were dramatically reduced, about 10%–15%, at the elevated flue gas temperature of 204°C (400°F) for all three configurations and for both Poplar River and Freedom coals, as compared to the 149°C (300°F) flue gas temperature.²⁹ An estimated 14.3% increase of sorbent usage is required to achieve collection efficiencies at a flue gas temperature of 204°C (400°F) similar to those at 149°C (300°F) for both the ESP-only and ESP–FF configurations. However, an estimated 70.7% increase in sorbent usage is needed for the FF configuration when the flue gas temperature was increased from 149° and 204°C (300° and 400°F). One partial explanation for the dramatic increase in carbon usage (70.7%) for the FF only at the flue gas temperature of 204°C (400°F) compared to 149°C (300°F) is the increased pulse rate at higher temperatures (increased A/C ratio) for the FF containing ash and carbon.

Sorbent size is another important parameter for mercury removal in flue gas, especially when mass transfer is an issue. Both the standard and fine MVD (of 20 and 5 µm, respectively) activated Luscar char were injected ahead of the ESP at different rates to examine the corresponding mercury removal efficiencies. The experimental data presented in Figures 3 and 4 show that a reduction

in sorbent size did not consistently result in improved mercury capture. At injection rates of >8 lb/Macf, the fine activated Luscar char provides much better ESP mercury removal than that achieved with the more coarse carbon for the Poplar River coal. On the contrary, a reduction in carbon size did not greatly enhance ESP mercury capture in the Freedom coal flue gas. There may be several reasons that caused this inconsistency, such as adhesive agglomeration of the fine sorbent, inconsistency in fineness, poor dispersion of the fine sorbent into the flue gas, etc. More effort is needed before final conclusions can be drawn.

Two different bag materials, Ryton® and Gore-Tex®, were tested in the FF-only case at 149°C (300°F). Based on limited test data as shown in Figure 3, the differences in the FF material, Ryton® versus Gore-Tex®, did not significantly affect mercury capture efficiencies.

The FF was operated at A/C ratios of 6 and 12 with the TOXECON™ configuration to evaluate the impact that increased flows may have on mercury capture. Based on limited tests, the observed differences between 6 and 12 did not appear to be significant with regard to mercury capture. In other words, the increased velocity did not appear to impact mercury removal. Overall, the mercury removal was less when the A/C was 12, mainly due to increased pulsing frequency. This increased frequency translated to poorer utilization of the PAC at a given injection rate. Because the tests were rather short, long-term effects, such as increased blockage, erosion rates, etc., could not be evaluated.

Future Tests. The EERC currently has plans to perform additional tests of additives on bench- and pilot-scale systems, as well as tests at other North Dakota power plants. As part of the second phase of this ongoing project, the applicability of the conclusions from the Phase I bench- and pilot-scale investigations will be evaluated by performing similar PAC injection and flue gas and fly ash measurements at a utility host site equipped with a slipstream FF installed downstream of existing ESPs. Sorbent injection upstream of a pulse-jet-type FF (TOXECON™) is the mercury control technology that will be field-tested at the Poplar River Power Station, which is owned and operated by SaskPower. Activities planned for the field demonstration at the Poplar River Power Station include field-testing a slipstream-scaled version of the TOXECON™ technology, preparing the site and installing the appropriate technology hardware, evaluating sorbent impacts and performance, assessing technology impact on unit operations, assessing ash reuse and disposal impacts, and estimating costs to control mercury. The results from Phase II of the project should provide the lignite industry with a technology option that can be considered by other utilities as they develop their own mercury control strategies. In addition, Phase II data will provide insights into mercury control effectiveness for other coals and particulate control configurations.

Conclusions

The activated (800°C, 1472°F) Luscar char and DARCO FGD were selected for additional testing in a 580-MJ/hr (550,000-Btu/hr) pulverized coal-fired unit, based on sorbent screening results, costs, and consensus among project sponsors. The following variables that could potentially affect mercury emission control were tested: lignite coal source (Poplar River or Freedom Mine), control device type (ESP, FF, ESPBFF, and Advanced Hybrid™ filter), FF type (Gore-Tex® or Ryton®), sorbent type (steam-activated [800°C, 1472°F] Luscar char and DARCO FGD) and particle size (approximate MVDs of 20 and 5 µm), sorbent injection rate, SEA use, mercury speciation, and flue gas temperature in the pollution control device. Pilot-scale test results indicated the following:

- \$ The relative proportions of Hg^0 , Hg^{2+} , and $\text{Hg}(\text{p})$ in the Poplar River and Freedom coal combustion flue gases were very similar at approximately 85%, 15%, and <1%, respectively.
- \$ The relative mercury removal efficiencies of the four control device technologies tested were 1) TOXECONTM and Advanced HybridTM filter, 2) FF, and 3) ESP, with the performance varying depending on coal and sorbent injection method.
- \$ The pilot-scale results on lignite showed an increase in the required PAC needed for similar removals when compared to full-scale data for eastern bituminous coals.
- \$ Most chlorine additives were effective in enhancing the mercury removal of activated carbon, thereby reducing the amount of sorbent needed to achieve a given level of mercury emission control. However, the use of HCl in the upper furnaces was not found to be effective.

Acknowledgments. This investigation was supported by a consortium of Environment Canada; SaskPower; Basin Electric Power Cooperative; Luscar Ltd.; Minnkota Power Cooperative; North Dakota Industrial Commission (NDIC); Otter Tail Power Company; EPRI; Great River Energy; Minnesota Power, Inc.; and Xcel Energy through the EERC's Jointly Sponsored Research Program, which is supported by the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) under Cooperative Agreement No. DE-FC26-98FT40321. We are grateful to the following colleagues and organizations for their support and advice: Lynn Brickett (DOE NETL), Don Rose (Environment Canada), Dave Smith (SaskPower), Vernon Laning (Basin Electric Power Cooperative), Bob Engler (Luscar Ltd.), Luther Kvernem (Minnkota Power Cooperative), Harvey Ness (NDIC), Terry Graumann (Otter Tail Power Company), Ramsey Chang (EPRI), Mark Strohfus (Great River Energy), Tim Hagley (Minnesota Power, Inc.), and Lee Eberley (Xcel Energy).

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Novel Nanoporous Sorbents for Removal of Mercury

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Introduction

There is a significant need for a technology to effectively remove mercury from aqueous effluents of coal-fired power plants such as, blow down water, wet scrubber effluents, and ash pond waters. These effluents typically contain high concentration of dissolved major and dissolved toxic constituents, and exhibit a wide range of pH values (~4 – 12 SU). During the last few years, we have designed and developed a new class of high-performance sorbent material for removing toxic constituents such as mercury from water and waste water. This novel material is created from a combination of a synthetic nanoporous ceramic substrate that had a specifically tailored pore size (~6.5nm) and very high surface areas (~900 m²/g) with self-assembled monolayers of well-ordered functional groups that have high affinity and specificity for specific types of free or complex cations or anions. Detailed descriptions of the synthesis, fabrication, and adsorptive properties of these novel materials have been published previously¹⁻³. We conducted a series of tests to evaluate the effectiveness of a synthetic novel sorbent for removing mercury from coal-fired power plant effluents.

Experimental

The novel substrates were prepared *via* a surfactant templated synthesis. The resulting siliceous structure was calcined to obtain a ceramic substrate with average pore size of 6.5 nm. Mercury is a very soft Lewis acid, and hence, both kinetically and thermodynamically “prefers” to undergo reaction with soft bases, such as thiols. Therefore, we functionalized the pores of the substrate with self-assembled monolayers of alkylthiols (Figure 1). The resulting mercury-specific adsorbent (thiol-SAMMS – thiol Self Assembled Monolayers on Mesoporous Silica) was tested to evaluate its adsorption capacity, specificity, and kinetics. Tests were conducted to: 1) evaluate the adsorption performance over a range of pH and ionic strengths of contacting solution, 2) determine the effects of equimolar concentrations competing cations on Hg-adsorption at two different pH values and, 3) assess the leachability of mercury-loaded SAMMS material using the Toxicity Characteristics Leaching Procedure (TCLP) of U. S. Environmental Protection Agency (USEPA).

A bench-scale treatability test was conducted to evaluate the mercury adsorption performance of thiol-SAMMS from a condensate waste stream. The principal dissolved components in this alkaline waste stream (pH: 8.5) consisted of mainly sodium borate (~30 mM), and sodium fluoride (~9 mM) with minor concentrations of sodium chloride (~3 mM), sodium nitrite (~0.9mM), sodium sulfate (~0.8mM), sodium nitrate (~0.6mM) and sodium iodide (~0.2 mM). The mercury concentration in solution was measured to be 4.64 mg/L. Trace concentrations (<2 mg/L) of Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mo, Ni, PO₄, Pb and Zn were also detected in this waste stream. To test the effectiveness of thiol-SAMMS in adsorbing mercury from this complexing matrix, thiol-SAMMS (Solution to solid ratio 1250 ml/g) was reacted with the waste solution for 8 hours.

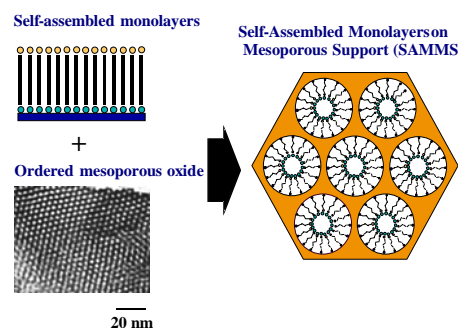


Figure 1. Technological basis of novel nanoporous sorbents

Results and Discussion

Adsorption of mercury by thiol-SAMMS showed a good fit to Langmuir isotherm (Figure 2). From the fitting parameters, the adsorption maximum was calculated to be 625 mg of Hg/g of sorbent, and the Langmuir constant was estimated to be 0.107 l/mg.

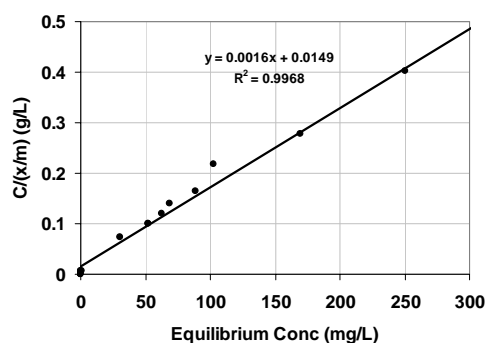


Figure 2. Langmuir Isotherm for Hg Adsorption by thiol-SAMMS

The kinetic data indicated (Figure 3) that adsorption was relatively rapid with ~99% dissolved mercury being adsorbed within the initial five minutes. Results of the TCLP (Toxicity Characteristics Leaching Procedure) tests indicated that Hg-adsorbed by the thiol-SAMMS was highly resistant to leaching (Figure 4).

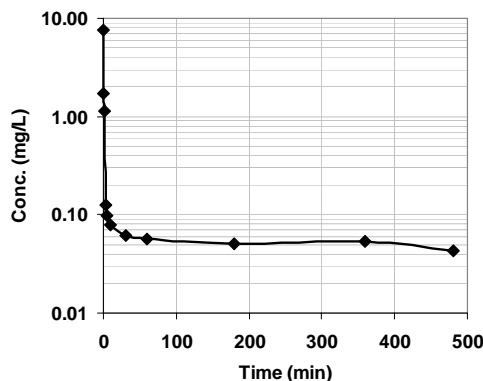


Figure 3. Kinetics of Hg Adsorption by thiol-SAMMS

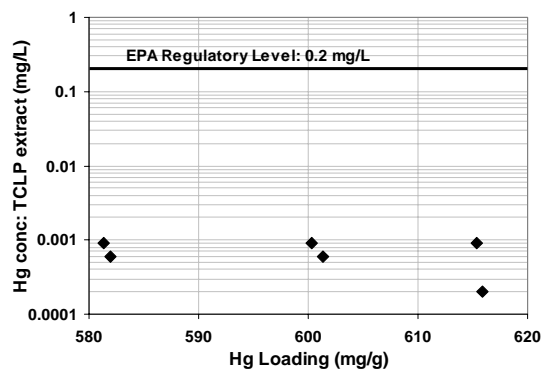


Figure 4. Leach Resistance of Hg-loaded thiol-SAMMS

Variation in pH or ionic strength did not significantly affect the Hg-adsorption affinity of thiol-SAMMS substrate (Table 1). The data showed (Table 2) that the presence of equimolar concentrations of competing cations at both pH values (4 and 7) did not significantly affect the specific adsorption of mercury. These data confirmed that mercury-thiol interaction being a soft acid-base interaction is both kinetically and thermodynamically a preferred reaction thus would not be significantly affected by pH, and the presence of competing cations in solution.

Table 1. Effect of pH and Ionic Strength

pH	K_d (ml/g)	NaNO ₃ (M)	K_d (ml/g)
2	9.9×10^5	0.0	5.5×10^7
3	1.4×10^6	0.1	3.5×10^7
4	1.7×10^7	0.3	3.3×10^7
5	1.7×10^7	0.6	2.4×10^7
7	3.9×10^7	2.0	5.5×10^7
8	4.8×10^7	3.0	5.3×10^7
10	7.6×10^6	4.0	5.6×10^7

Table 2. Effect of pH and Competing Cations

pH	Cations	K_d (ml/g)
4	Na	1.5×10^7
4	Ca, Cu(II), Fe(II), Pb	1.0×10^7
4	Ca, Cd, Cu(II), Fe(II), Ni, Pb, Zn	1.0×10^7
7	Na	3.9×10^7
7	Ca, Cu(II), Fe(II), Pb	1.1×10^7
7	Ca, Cd, Cu(II), Fe(II), Ni, Pb, Zn	4.5×10^7

The data from the bench scale test of the condensate waste stream indicated that thiol-SAMMS had adsorbed ~98.9% of the mercury initially present in this solution (residual mercury concentration 0.052 mg/L). This solution contained ~0.2 mM of iodide, a strong mercury complexing ligand and the speciation calculations indicated that all the soluble mercury existed in the form of iodide complexes (HgI_2^0 : ~52%; HgI_3^- : ~47%, and HgI_4^{2-} : ~1%). These results confirmed previous observation⁴ that thiol-SAMMS can effectively remove iodide-complexed mercury from solutions.

Acknowledgement. This study was supported by the Office of Science and Technology of the U. S. Department of Energy. Pacific

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COMPARISON OF SORBENTS AND FURNACE ADDITIVES FOR MERCURY CONTROL IN LOW-RANK FUEL COMBUSTION SYSTEMS

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Introduction

North Dakota lignite-fired power plants have shown a limited ability to control mercury emissions in currently installed electrostatic precipitators (ESPs), dry scrubbers, and wet scrubbers (1). This low level of control can be attributed to the high proportions of Hg^0 present in the flue gas. Speciation of mercury in flue gases analyzed as part of the EPA information collection request (ICR) for Hg data showed that Hg^0 ranged from 56% to 96% and the oxidized Hg ranged from 4% to 44%. The Hg emitted from power plants firing North Dakota lignites ranged from 45% to 91% of the total Hg, with the emitted Hg being greater than 85% elemental. The average emitted from North Dakota power plants was 6.7 lb/TBtu (1, 2).

The composition of a coal has a major impact on the quantity and form of Hg in the flue gas and, as a result, on the ability of air pollution control devices (APCDs) to remove Hg from flue gas. In general, North Dakota lignite coals are unique because of a highly variable ash content, ash that is rich in alkali and alkaline-earth elements, with high oxygen levels, high-moisture levels, and low chlorine content. Experimental results indicate that low-chlorine (<50-ppm) coal combustion flue gases (typical of North Dakota lignite) contain predominantly Hg^0 , which is substantially more difficult to remove than Hg^{2+} (3). The generally high calcium contents of lignite coals may reduce the oxidizing effect of the already low chlorine content by reactively scavenging chlorine species (Cl , HCl , and Cl_2) from the combustion flue gas. The level of chlorine in flue gases of recently tested North Dakota and Saskatchewan lignites ranged from 2.6 to 3.4 ppmv, with chlorine contents ranging from 11 to 18 ppmw in the coal on a dry basis, respectively.

The technologies utilized for the control of Hg will ultimately depend upon the EPA-mandated emission limits. The strategies include sorbent injection with and without enhancements upstream of an ESP or fabric filter (FF) and Hg oxidation upstream of a wet or dry flue gas desulfurization system (FGD). The new technologies being investigated include Hg capture using the Energy & Environmental Research Center's (EERC) advanced hybrid particulate collector (AHPC) or the *Advanced Hybrid™* gold-coated materials, baghouse inserts, and carbon beds (4).

Sorbent injection for removing Hg involves adsorption of Hg species by a solid sorbent injected upstream of a particulate control device such as a FF (baghouse) or ESP. Many potential Hg sorbents have been evaluated (4). These evaluations have demonstrated that the chemical speciation of Hg controls its capture mechanism and ultimate environmental fate. Activated carbon injection is the most mature technology available for Hg control. Activated carbons have the potential to effectively sorb Hg^0 and Hg^{2+} but depend upon the carbon characteristics and flue gas composition (4). The projected annual cost for activated carbon adsorption of Hg in a duct injection system is significant. Carbon-to-mercury weight ratios of 3000:18,000 (lb carbon injected/lb Hg) in flue gas have been estimated to achieve 90% Hg removal from a coal combustion flue gas containing 10 $\mu\text{g}/\text{Nm}^3$ of Hg (5).

Mercury oxidation technologies being investigated for Fort Union lignites include catalysts, chemical agents, and cofiring materials. The catalysts that have been tested include a selective catalytic reduction (SCR) catalyst for NO_x reduction, noble metal-impregnated catalysts, and oxide-impregnated catalysts. The chemical agents include chlorine-containing salts and cofiring fuels that contain oxidizing agents (6).

Mercury oxidation catalysts have shown high potential to oxidize Hg^0 . Results in testing a slipstream at a North Dakota power plant indicated over 80% conversion to oxidized Hg for periods of up to 6 months (6). Tests were also conducted using iron oxides and chromium, with little success of oxidation. Galbreath and others (7) have conducted short-term pilot-scale testing with maghemite ($\gamma\text{-Fe}_2\text{O}_3$) additions and were able to transform about 30% of the Hg^0 in North Dakota lignite combustion flue gases to Hg^{2+} and/or $\text{Hg}(\text{p})$ and, with an injection of a small amount of HCl (100 ppmv), nearly all of the Hg^0 to Hg^{2+} . Theoretically, the use of chloride compounds to oxidize Hg^0 to Hg^{2+} makes sense. The evidence includes chemical kinetic modeling of bench-scale test results indicating that the introduction of chloride compounds into the high-temperature furnace region will most likely result in the production of atomic chlorine and/or molecular chlorine, which are generally thought to be the dominant Hg^0 reactants in coal combustion flue gases (4).

The overall purpose of this research is to develop advanced, innovative Hg control technologies to reduce Hg emissions by 50% to 90% in flue gases typically found in North Dakota lignite-fired power plants at costs of one-half to three-fourths of current estimated costs. The specific objectives are focused on determining the feasibility of the following technologies: Hg oxidation for increased Hg capture in dry scrubbers and the use of Hg adsorbents with a baghouse.

Experimental

The pilot-scale evaluations of sorbent injection and sorbent-enhancement agents (SEA) were performed using the EERC's particulate test combustor (PTC) equipped with several particulate control options to evaluate Hg sorbent effectiveness in coal combustion flue gases. Initial tests included a comparison of particulate control technologies with the same sorbents and SEAs. The second phase of the research is focused on evaluating various sorbents and SEAs for Hg control effectiveness in conjunction with the ESP-only configuration.

The PTC is a 550,000-Btu/hr (580-MJ/hr) pc-fired unit designed to generate fly ash and flue gas chemistry representative of that produced in a full-scale utility boiler. Coal is introduced to the primary air stream via a screw feeder and ejector. An electric air preheater is used for precise control of the combustion air temperature. The PTC instrumentation permits system temperatures, pressures, flow rates, flue gas constituent concentrations, and baghouse- or ESP-operating data to be monitored continuously and recorded on a data logger. Two PSA Sir Galahad atomic fluorescence-based continuous mercury monitors (CMMs) were located upstream of the sorbent injection point and at the particulate control device outlet to monitor Hg vapor concentrations continuously throughout the tests. Wet chemistry samples were collected using ASTM Method D6784 (Ontario Hydro Method) to verify CMM measurement and performance of the sorbents with SEA injection.

Freedom coal with a mean Hg content of 0.05 $\mu\text{g}/\text{g}$ was combusted at the nominal rate of 80 lb/hr. Based on the CMM data, the total Hg vapor concentration (Hg_{gas}) upstream of sorbent injection varied from 7.0 to 9.2 $\mu\text{g}/\text{m}^3$. The mean flue gas stream Hg level was $7.6 \pm 0.5 \mu\text{g}/\text{m}^3$ in dry flue gas, 3% O_2 . The mean elemental Hg vapor content (Hg^0) was about 6.8 $\mu\text{g}/\text{m}^3$.

Two forms of Hg removal were evaluated—sorbent injection only and sorbent injection with SEAs. SEAs were added to the coal prior to introduction to the furnace. Sorbents were injected upstream of the ESP using a dual-screw K-Tron feeder. The feeder was calibrated prior to the start of sorbent injection. In addition, the weight of sorbent added during a day was divided by the time of injection to provide a mean feed rate. Average feed rates ranged from 3.75 to 15 lb C/MMacf.

Results and Discussion

The results of the addition of materials with coal at very low levels along with the activated carbon injection (Norit DARCO FGD®) upstream of an ESP–FF (TOXECON™, *Advanced Hybrid™* filter, and ESP only) are illustrated in Figure 1. The first part of the figure shows the baseline data for Hg emissions ranging from 9 to 12 $\mu\text{g}/\text{Nm}^3$, with 80% to 90% of the Hg in the elemental form. The second case is activated carbon injection alone and with the addition of SEA 2, showing a reduction in Hg emissions to 90% removal. The third case is the *Advanced Hybrid™* filter alone and with the addition of SEA 2, which produced nearly 90% control efficiency. The final ESP-only case also indicated up to 90% control. The control efficiency for the ESP-only case showed significant potential improvement over past results obtained with the ESP only. All three configurations performed significantly better in Hg control with the combination of sorbent injection and SEAs added to the feed coal.

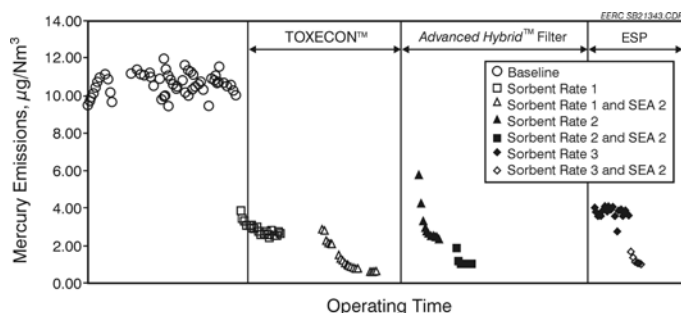


Figure 1. Mercury emissions for activated carbon injection combined with an SEA additive using various particulate control devices.

The second phase of testing included activated carbon sorbent injection and SEA upstream of an ESP for control of Hg emissions from North Dakota lignite. The testing was conducted using the EERC PTC equipped with an ESP only. The results of the first tests are illustrated in Figure 2. Figure 2 shows the inlet total Hg level at 9 $\mu\text{g}/\text{m}^3$ and baseline outlet (initial and final) at 7.2 $\mu\text{g}/\text{m}^3$. Norit DARCO FGD® activated carbon was injected at 3.75 and 15 lb C/MMacf, resulting in 50% to 60% Hg reduction. The addition of SEA with the coal and injection of 3.75 lb C/MMacf resulted in a reduction of over 70% of the Hg emissions.

Conclusions

The comparison tests show that Hg emissions from lignite-fired combustion systems can be reduced significantly using a variety of particulate control devices. Two different ESP–baghouse combinations and the ESP-only configuration were capable of controlling up to 90% of the gaseous Hg emissions when activated carbon sorbent injection was combined with Hg oxidant addition to the coal. This is particularly significant in the case of the ESP-only configuration, as many of the lignite-burning units are currently

equipped with this configuration. This technology also has the potential to improve dry FGD baghouse control efficiency. While the

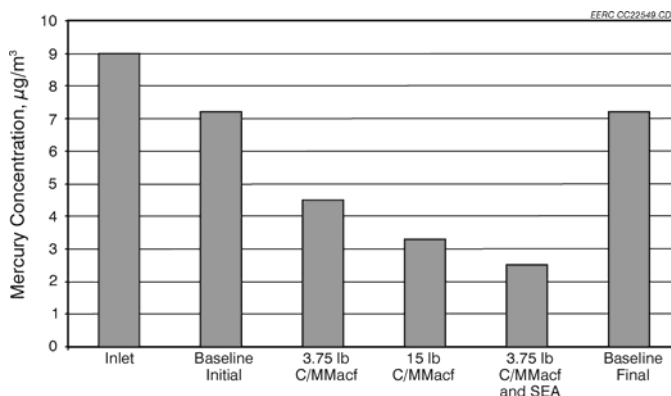


Figure 2. ESP mercury concentrations as a function of sorbent and SEA additive for a North Dakota lignite.

results to date demonstrate effective Hg removal across the ESP, optimization of sorbents and SEA types and the addition ratios is essentially to develop the most cost-effective plan for controlling Hg emissions.

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MERCURY CONTROL USING COMBUSTION STAGING

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Introduction

In December 2000, the U.S. EPA reported that mercury (Hg) emissions from coal-fired power plants pose significant hazards to public health and must be reduced. The EPA is under court order to propose Hg regulations for coal-fired power plants in 2003 and finalize them in 2004. Present regulatory mechanisms require that such regulations be developed through Maximum Achievable Control Technology (MACT). Several other frameworks for Hg regulations have been proposed recently. The Clear Skies Initiative proposed by President Bush mandates dramatic reductions in power plant SO₂, NO_x, and Hg emissions over the next 15 years. Independent of the EPA's final decision regarding the required level of Hg control, important questions that need immediate answers are (1) what technologies can provide a significant level of Hg removal and (2) can a significant level of Hg removal be achieved for all coal types?

Many utilities are actively seeking effective and inexpensive technologies for controlling multiple pollutants emitted from power plants. Recent experimental data^{1,2,3} obtained by EER demonstrated the reduction of Hg emissions through the use of fly ash with high carbon content formed "*in situ*" in the combustion process of coal-based power generating stations. High-carbon fly ash can be formed by low NO_x burners (LNB), overfire air (OFA) injection or in coal reburning. These commercial technologies are currently used to reduce NO_x emissions from coal-fired power plants.

This paper further investigates potential of using high carbon fly ash for Hg control. Objective of this work was to investigate effects of carbon in ash, coal composition, and temperature on the efficiency of Hg removal.

Experimental Facility

Tests on utilization of "in-situ" formed high-carbon fly ash to remove Hg from flue gas were conducted in Boiler Simulator Facility (BSF) described elsewhere⁴. The BSF has a full load firing capacity of 1×10⁶ Btu/hr and is designed to provide an accurate sub-scale simulation of the flue gas temperatures and composition found in a full-scale boiler. A schematic of the BSF and setup for Hg sampling are shown in Figure 1. The BSF consists of a burner, vertically down-fired radiant furnace, horizontal convective pass, and ESP. A variable swirl diffusion burner with an axial fuel injector is used to simulate the approximate temperature and gas composition of a commercial burner in a full-scale boiler. Numerous ports located along the axis of the facility allow access for supplementary equipment such as reburning and OFA injectors, and sampling probes.

The cylindrical furnace section is constructed of eight modular refractory lined sections with an inside diameter of 22 inches. The convective pass is also refractory lined, and contains air cooled tube bundles to simulate the superheater and reheater sections of a utility boiler. Heat extraction in the radiant furnace and convective pass can be controlled such that the residence time-temperature profile matches that of a typical full-scale boiler. A suction pyrometer is used to measure furnace temperatures.

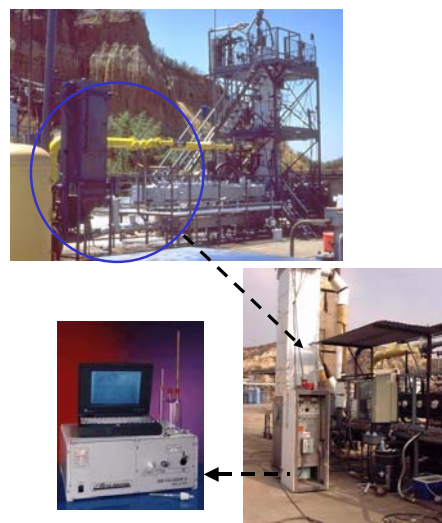


Figure 1. Boiler Simulator Facility.

High-carbon fly ash was formed using air staging. An online Hg analyzer from PS Analytical was used in these tests. The analyzer is capable measuring both total (Hg) and elemental (Hg⁰) mercury in flue gas. Mercury concentration in flue gas was measured at ESP inlet and outlet. The ESP for the BSF is a single-field down-fired unit consisting of 12 tubes with axial corona electrodes. The ESP flue gas temperature was controlled by inserting or removing cooling rods situated in the convective pass.

Experimental Results

Objective of pilot-scale testing were to determine effects of combustion staging and ESP temperature on efficiency of Hg removal by fly ash. Tests were conducted with several bituminous coals. Carbon in fly ash (characterized as LOI) was adjusted by staging combustion. Two approaches to stage combustion were used – air staging (overfire air injection or OFA) and fuel staging (reburning). In air staging part of the combustion air is redirected from the main combustion zone into post-combustion zone (overfire zone). Because fuel combustion in air staging occurs in fuel-rich environment, fly ash tends to have higher carbon content than that at typical combustion conditions. Process variables in air staging tests included location of overfire air injection and stoichiometric ratio in the main combustion zone (SR₁). Stoichiometric ratio at the furnace exit (SR₃) in all tests was 1.16 which corresponded to about 3% excess air in flue gas.

In reburning part of the fuel (typically 10-30% of total) is injected above the existing burner zone to produce a slightly fuel-rich environment. Overfire air is injected downstream of the reburning zone to complete fuel combustion. Process variables in reburning tests were amount of the reburning fuel and the flue gas temperature T_{OFA} at which overfire air was injected (T_{OFA} was in the range of 1800-2500 °F). The latter was achieved by changing location of the overfire air injection port.

Figure 2 shows dependence of Hg removal efficiency (defined as a difference between Hg introduced with coal and Hg concentration in the gas phase at ESP outlet) as a function of LOI in air staging. Temperature of flue gas in ESP in these tests was 350 °F. Figure 2 demonstrates that mercury removal efficiency increases with LOI increase. Efficiency of Hg removal also depends on coal properties, especially for LOI up to 4%. Maximum Hg removal efficiency achieved in air staging tests was ~60%.

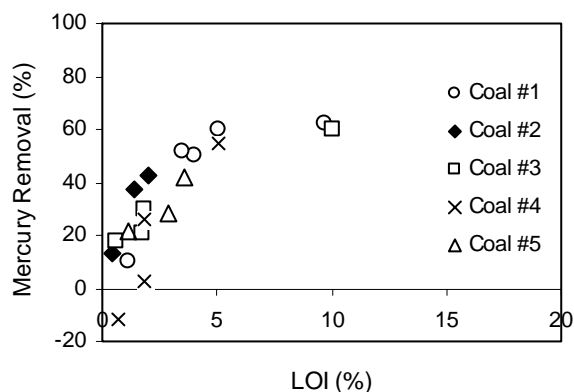


Figure 2. Effect of LOI on Hg removal in air staging.

Figure 3 shows effects of LOI and ESP temperature on Hg removal in reburning for coal #3. Figure 3 demonstrates that efficiency of Hg removal increases with increase in LOI and decrease in ESP temperature. Maximum Hg removal efficiency achieved in reburning tests was about 85%.

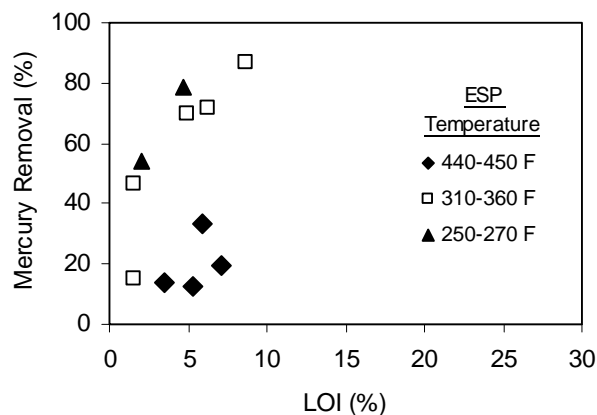


Figure 3. Effect of LOI on Hg removal in air staging for coal #3.

Consol studied⁵ effect of ESP temperature on Hg removal on Hg adsorption on fly ash. In these tests high carbon fly ash generated by combustion of bituminous coal was re-injected into the duct of 1.5 MBtu/hr combustor. The flue gas temperature was controlled using both duct humidification and the pilot plant heat exchange. Amount of re-injected fly ash was similar to that generated by combustion of a bituminous coal. Results of the Consol study were combined with present data to determine dependence of Hg adsorption on temperature. Based on these data, transfer function was developed that predicted dependences of the efficiency of Hg adsorption on fly ash on LOI and temperature. Figure 4 shows results of the present and Consol studies (symbols) as well as predictions of the transfer function (lines). Figure 4 shows good agreement between experimental data and modeling predictions.

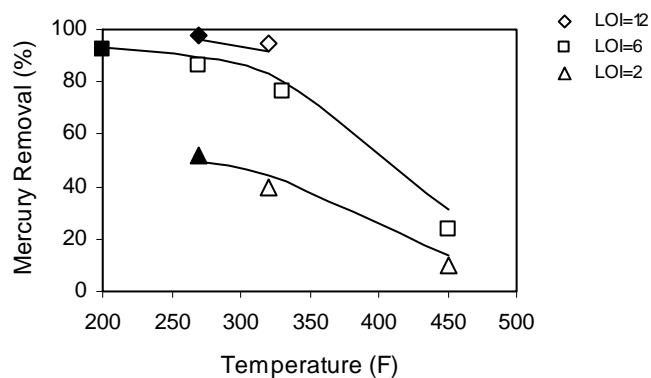


Figure 4. Experimental data (symbols) and modeling predictions (lines) on the effect of temperature on Hg adsorption of fly ash. Solid symbols represent Consol data, open symbols present study.

Figure 5 shows comparison of experimental data for reburning (Figure 3) adjusted to 350 °F using transfer function with predictions of the transfer function. Figure 5 demonstrates relatively small scatter of experimental data. It also demonstrates that about 80% Hg adsorption on fly ash can be expected at LOI 7-9% and ESP temperature of 350 °F.

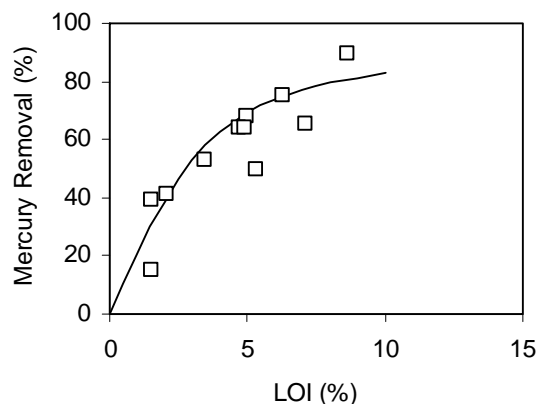


Figure 5. Comparison of experimental data and modeling predictions on the effect of LOI on Hg removal at 350 °F.

Figure 6 shows predicted by transfer function effect of temperature on Hg adsorption on fly ash. Figure 6 suggests that both temperature and LOI should be considered in selecting optimum conditions for Hg removal: LOI change in the range of 2-8% offers most significant effect on Hg removal. LOI increase to 12% gives only marginal improvement in Hg reduction efficiency. Temperature decrease below acid dew point can result in sulfuric acid condensation and duct corrosion. While acid dew point depends on a number of parameters including coal sulfur content, in most cases it is lower than 290 °F. Figure 6 suggests that Hg removal efficiency at LOI = 8-12% can be 80-90% at temperatures above 290 °F.

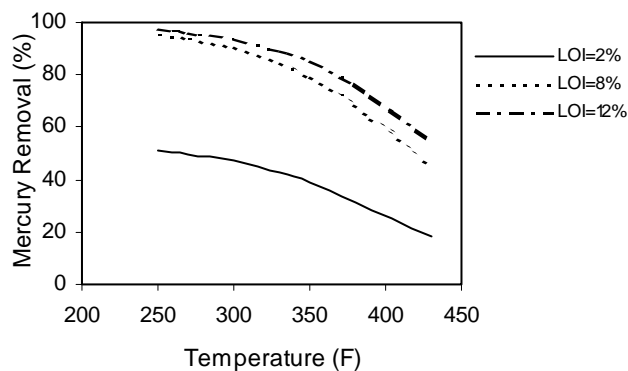


Figure 6. Predicted effect of temperature on Hg removal.

Conclusions

Experimental results confirmed that air staging and reburning could be used to control Hg emissions from coal-fired boilers. Pilot-scale testing demonstrated that this approach can provide 80-90% Hg removal across an ESP for bituminous coals at LOI = 8-12%. Lowering ESP temperatures can further improve Hg removal.

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ELEGANT ELUSIVE OXIDATION MECHANISM OF MERCURY

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Introduction

Although the levels of mercury in coal generally are small (0.1-1.0 parts per million by weight (ppmw)), the United States alone currently burns about 900 million tons/year. The problem with combustion or incineration of any material containing traces of mercury is that all the mercury volatilizes as atomic elemental mercury and none is retained in any bottom ash. This applies even to crematoria. The behavior stems from its unusual chemistry. Mercury has no condensed phase molecules that are stable above about 600-700 °C. This is partly why liquid mercury, quicksilver, was discovered in ancient times and is documented by the Phoenicians and Carthaginians. It is easily obtained from its ore cinnabar, HgS, solely by heating in air. Also, the thermal instability of mercuric oxide, HgO, helped Priestley discover oxygen. Even in the gas phase, the only molecule of mercury with significant stability is mercuric dichloride. As a result, what is observed in combustion or other high temperature systems is that the majority of the mercury in the exhaust is atomic. Because of this, and the fact that liquid mercury is very volatile, it is difficult to capture mercury with conventional type ab- or adsorption techniques¹. Although the formation of the dichloride is thermodynamically favored, there are no direct kinetic channels for its production. Even so, in practice a small and unpredictable fraction of the mercury is exhausted as the dichloride, the two constituting the mass balance of mercury in the system. This partial conversion or oxidation as it is generally referred to, is extremely intriguing and has never been understood. Its important practical significance stems from the fact that whereas atomic mercury is very difficult to capture, the dichloride is readily soluble in water and so can be removed and processed by the already present water scrubbers. Consequently the more mercury present as the dichloride in an exhaust, the less is emitted to the atmosphere.

Extensive gas phase kinetic modeling studies over many years have failed to adequately describe this formation of the dichloride². The dilemma is that its formation has to occur via the monohalide, HgCl. This is chemically weakly bound and will be very short-lived at temperatures much above 400 °C. Consequently, there are very restrictive constraints imposed on the gas phase chemistry. The temperatures can not be too high or molecular formation is not possible and when they fall low enough the kinetic reaction rates are beginning to freeze because of activation energy barriers. The temperature, time and concentration limitations prove to be very severe in practical combustion systems and the modeling is clearly inadequate in predicting the fractional distribution of mercury between the element and the dichloride. The majority of gas kineticists now acknowledge this fact³ and conclude that the system is "complex"⁴. In reality, the value of these modeling studies has been two-fold. Firstly, they have established that the gas phase chemistry can only be marginally involved, if at all, in the conversion of atomic mercury to its dichloride. Secondly, they provide a useful reminder to all of us not to hold too firmly to preconceived ideas.

Full-scale combustor observations have never been able to correlate the observed fractional conversion to the dichloride with any operational parameter. Recently, however, it has been increasingly clear that blowing fly ash or particles into the flue gases does enhance the production of the dichloride⁵.

A very recent review assesses the current status of all the control options currently being tested by the coal industry¹. However, the conclusion remains that no method has yet proven to be generally successful or economically attractive.

In previous studies in this laboratory it was found if sodium and sulfur are present in flame gases at very low levels (ppmv) that sodium sulfate forms very efficiently not in the burned gases but on any cooler surface intercepting the flow^{6,7}. The reduced dimensionality of the surface, 2-D instead of that of the 3-D gas phase, appears to be very important in facilitating the process as well as changing the chemistry from the gas phase to the condensed phase regime. It was also noted in that work that concepts such as dew point lose all meaning. Because of this experience, and having the experimental system available, it was decided to run test experiments with mercury. These introduced low levels of mercury (ppmv), sulfur and chlorine into flames, the burned gases of which were then intercepted by a cooled probe at various temperatures.

Experimental

Deposition Methods

Cylindrical propane or hydrogen, oxygen, nitrogen flames have been burned on a well-characterised flat flame burner. Mercury was introduced as a fine aqueous aerosol of either its nitrate or acetate solution from an ultrasonic nebulizer such that its flame concentration was in the range of 5-30 ppmv⁶⁻⁸. Small quantities of SO₂, HCl or Cl₂ could be added from certified gas mixtures, or alternately via the nebulizer in the form of their appropriate salt solutions. Several cylindrical collection probes were used of either Inconel-600 stainless steel or tightly clad with platinum foil. Air or water internally cooled these and a thermocouple was built into their wall thickness.

Two types of experiments have been accomplished. Those in the hotter burned gases used cooled probes. Such studies are highly quantitative and have resolved the nature of mercury's heterogeneous chemistry and its dependence on the variables in the system. Important additional experiments that relate to cooler downstream flue gas temperatures and industry also were undertaken to simulate the mercury behavior in practical systems. In these cases the probe was located downstream where the burned gas temperature has decayed to about 200 °C or less. In such experiments an electrically internally heated collection probe was used to maintain a desired probe surface temperature.

Characterization Methods

Four powerful modern analytical systems have helped to fully characterize these observed deposits. These are a Nicolet Fourier Transform Raman Spectrometer, a Bruker High Temperature Powder x-ray Diffractometer, a Thermo Jarrell Ash Inductively Coupled Plasma/Atomic Emission Spectrometer (ICP/AES), and a Mettler Thermogravimetric Analyser. By this means the chemical composition of deposits and their quantitative rates of deposition have been accurately measured. In all, over two hundred experiments now have been studied involving mercury deposition.

Results

From the very first experiment, it was apparent that mercury has a significant propensity for heterogeneous deposition. Provided that the probe temperatures are within a desirable temperature window, deposits are obtained with a formation efficiency that is essentially the same as with alkali metals. The deposits are molecular in nature. Figure 1 illustrates the Raman spectrum of such a deposit. It is immediately apparent that mercuric sulfate deposition is dominant if sulfur is present in the flame. However, the exact nature of the sulfate depends on the amount of sulfur in the flame. A ratio of sulfur

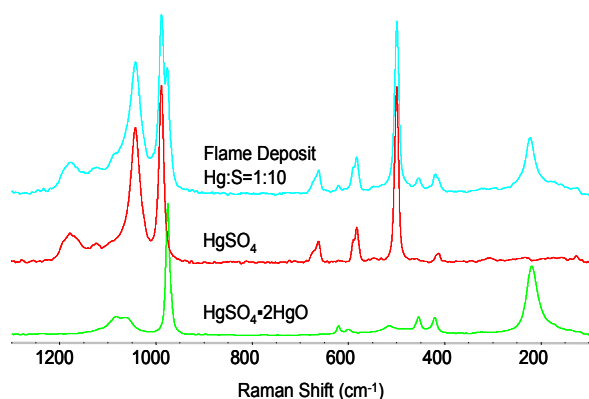


Figure 1. Raman spectrum of a deposit from the burned gases of a propane flame containing traces of mercury (25 ppmv) and sulfur. Compared to spectra of pure samples of mercuric sulfate and its basic sulfate, Schuetteite, $\text{HgSO}_4 \cdot 2\text{HgO}$.

to mercury of above 10-fold produces predominantly mercuric sulfate with the basic Schuetteite, $\text{HgSO}_4 \cdot 2\text{HgO}$, increasing as the ratio decreases. With no sulfur in the flame a brown deposit results that is pure HgO . These results are validated by auxiliary x-ray analyses of the deposits. As was seen with alkali deposition, the mercury illustrates a preferential ranking that appears to reflect thermodynamic stabilities. On reaching the surface it will make its favored molecule if possible but whether it be sulfate or oxide the rate of deposition remains the same. As indicated in Fig. 2, deposits of sulfate can be obtained in the hot burned gases of a flame over an extended range of temperatures.

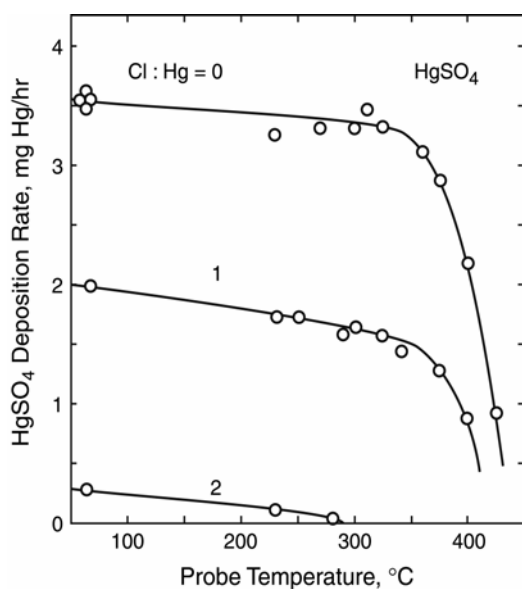


Figure 2. Rates of deposition of HgSO_4 as a function of probe temperature and flame chlorine content. Measurements in a fuel lean $\text{C}_3\text{H}_8/\text{O}_2/\text{N}_2$; 0.9/5/20 flame 12 ms downstream.

Precise additions of chlorine together with the mercury and sulfur indicate a quantitative reduction of the deposit. Experiments indicate that the chlorine in the flame as HCl vigorously attacks the sulfate deposit converting it to volatile $\text{HgCl}_2(\text{g})$ that sublims back into the gas flows. In normal coal combustors, the levels of impurities

generally are $\text{S} \gg \text{Cl} \gg \text{Hg}$. As a result, under the right conditions, this heterogeneous conversion will occur naturally. It represents the elusive chemical mechanism missing from models and explains the variability of the amount of $\text{HgCl}_2(\text{g})$ observed. Recent analyses

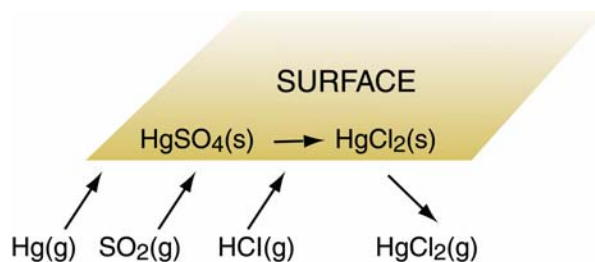


Figure 3. Heterogeneous mechanism whereby gaseous atomic mercury is efficiently converted to gaseous HgCl_2 .

suggest that the HCl directly ablates $\text{HgCl}_2(\text{g})$ from the sulfate and the step through the less stable $\text{HgCl}_2(\text{s})$ as indicated does not occur. In this way, the mercury uses the surface as a catalytic means whereby it can satisfy its thermodynamic desire to convert to the stable dihalide.

Flue Gas Measurements and Mercury Control

To confirm the generality of this heterogeneous formation of HgSO_4 an internally heated stainless steel probe was positioned downstream in burned gases where mixing had cooled the flows to 200°C or less. Deposits again were obtained however their formation window was narrowed. Temperatures in the range $150\text{--}250^\circ\text{C}$ were optimal. Moreover such deposits disappear if chlorine is present in the system. Additionally it is clear that these deposits once formed are stable and are only removed by HCl . They can be converted though to more stable mercury compounds. In other words if a sulfur free system is initially used the deposit is HgO . If a small amount of sulfur is added, this all changes to the basic sulfate and with more sulfur becomes the sulfate. Changes occur up the chain of preferential ranking but once converted the process is irreversible. It is clear that this is a dominant channel and an explanation of the role of fly ash or particle additions. A control method of solely providing adequate surface in the flue gases at the optimal surface temperature and ensuring adequate gas/surface collisions now is recommended⁹.

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Mercury Regulatory Policy and Electric Utilities

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Introduction

On December 15, 2003, Environmental Protection Agency (EPA) Administrator Leavitt signed the "Utility Mercury Reductions" proposal—the first-ever proposed rule to regulate mercury emissions from new and existing coal-based power plants and nickel emissions from new and existing oil-based power plants. The Utility Mercury Reductions proposal contains two alternative control plans—a market-based cap-and-trade approach and a Maximum Achievable Control Technology (MACT) standard. This paper will give a brief history, synopsis, and critique of this regulatory proposal, and how it compares to other proposed policies aimed at controlling mercury emissions from the electric utility industry.

Regulation of Power Plant Mercury Emissions

The Clean Air Act Amendments (CAAA) of 1990 authorize EPA to regulate mercury emissions and other air toxics from electric utilities, if necessary, to protect against specific threats to public health caused by these emissions. On December 14, 2000, EPA issued a "regulatory determination" under the Clean Air Act (CAA) that regulation of mercury is "appropriate and necessary" for coal- and oil-based power plants, and that certain other hazardous air pollutants (HAPs) pose a "potential concern for carcinogenic effects...[and] public health."¹ EPA listed coal-based power plants for regulation under §112(c) of the Clean Air Act—the list of source categories for which EPA must develop emissions standards based on the Maximum Achievable Control Technology (MACT). Under the MACT program, emissions restrictions based on the levels achieved in practice by the best performing 12 percent of plants must be applied to all existing plants.

The EPA regulatory determination noted, "there are uncertainties regarding the extent of the risks due to electric utility mercury emissions."² Previously, in its Mercury Research Strategy, in which EPA describes its strategic approach for its mercury research program through 2005, the agency stated that "[t]he amount of mercury deposited in the United States that can be directly attributed to domestic combustion sources remains uncertain."³ Notwithstanding these conclusions, EPA began to craft a proposed standard for mercury that would require MACT. Under the terms of a consent decree, EPA proceeded on a track to issue a proposed rule by December 2003, a final rule by December 2004, and to require compliance by December 2007.

The December 2000 regulatory determination limited the EPA Administrator's policy options, specifically with respect to implementing a flexible and cost-effective program. Electric utilities are explicitly treated differently under the CAA than other major sources of HAPs. Under §112(n)(1)(A) of the CAA, EPA is not required to regulate electric utility plants using the MACT program. As EPA stated, "if EPA determines that regulation of mercury emissions from electric utilities is necessary and appropriate, EPA would have the full set of regulatory tools available under §112 to address those emissions, including §112(f), as well as any alternative control strategies the Agency has identified in its Report to Congress."⁴

Mercury Emissions From Power Plants

Trace amounts of mercury are naturally present in coal. As a trace metal that is emitted during coal combustion, mercury is

transformed into three major chemical species: elemental, ionic (or oxidized), and particulate. The chemical species of mercury formed during the combustion process and post-combustion conditions vary significantly from one plant to another. Of the total mercury formed, the amount of elemental mercury varies from 10-90 percent. Elemental mercury usually travels great distances from its source, and can remain in the atmosphere for months to years. Ionic mercury is water soluble, and as such, falls or washes out of the air. Deposition of ionic mercury is typically in the local vicinity (50–100 km) of its source.

In order to assess mercury emissions from coal-based power plants, in 1998 EPA issued an Information Collection Request (ICR)⁵ that required owner/operators to report for calendar year 1999 the quantity of fuel consumed and the mercury content of that fuel. In addition, 84 plants were selected to measure flue gas mercury emissions and its chemical form. Based on analysis of the ICR data, EPA concluded that U.S. electric utilities release about 48 tons of mercury every year, which is roughly one-third of the total anthropogenic emissions of mercury in the United States, less than 10 percent of total North American emissions, and about one percent of total global mercury emissions.

Mercury Controls

A power plant which burns fossil fuels for the generation of electricity is typically equipped with a high-efficiency baghouse—fabric filter (FF)—or electrostatic precipitator (ESP) for particulate removal; staged-combustion burner configurations for low-nitrogen oxides (NO_x) emissions; and post-combustion flue gas treatment devices for NO_x and sulfur dioxide (SO₂) control—selective catalytic reduction (SCR) and selective noncatalytic reduction (SNCR) technologies for NO_x control, and high-efficiency flue gas desulfurization (FGD) scrubbers for SO₂ control. Not all power plants utilize all these control devices. For example, about 65 percent of plants use only an ESP, 10 percent use only a FF, and 25 percent use a combination of an ESP and wet FGD to control particulates; about 25 percent of plants use scrubbers and the rest either use low-sulfur coal or fuel-switch to control SO₂.⁶

Mercury control options are highly dependent on the existing power plant's design, operating characteristics, and fuel used—in the case of coal, the type of coal used is also important. Thus, potential mercury emissions are unique to each unit. For some plants, mercury emission reductions of 70–90 percent may be impossible to achieve. In addition, there is still considerable uncertainty in the measurement of mercury emissions, since mercury CEMs will most likely not be commercially available, accurate, or reliable within the next few years.

The characteristics of the coal-based plant that most affect emissions of mercury and the type of control technology used are the mercury content and other chemical aspects of the coal (particularly the chloride content); the boiler operating conditions; the design and operation of any particulate collection devices; the design and operation of any flue gas treatment systems; and the use of advanced NO_x removal technology, such as SCR and SNCR.

In addition to removing specific pollutants, such as fine particulates, SO₂, and NO_x, currently installed air pollution controls may also remove mercury. Measurements at a variety of U.S. power plants performed under EPA's mercury ICR indicate that existing emission control devices for particulates (fly ash) and SO₂ capture, on average, approximately 40 percent of the mercury present in the flue gas from burning coal, as well as a large amount of non-mercury HAPs. Mercury removal rates, however, varied from 0 to more than 90 percent among the power plants that were tested.⁷

EPA, DOE, and others are in agreement that the implementation of further controls for reducing SO₂ and NO_x as required in the proposed Interstate Air Quality Rule (IAQR), will result in significant additional reductions in mercury emissions. Focusing on these “co-benefits” of reduced mercury emissions also would allow adequate time for the development and commercialization of mercury control technologies that are currently in progress.

MACT Alternative Control Plan

One alternative control plan in the Utility Mercury Reductions proposal to set national emission standards for hazardous air pollutants (NESHAP) pursuant to §112 of the CAA. The proposed §112 MACT rule would require coal- and oil-based power plants to meet HAP emissions standards reflecting the application of the MACT determined pursuant to the procedures set forth in CAA §112(d).

In October 2002, the final report of the Utility MACT Working Group was submitted to the Clean Air Act Advisory Committee. This report included recommendations of the “Industry Stakeholder Group,” which comprised owners and operators of electric utility steam generating units from both the public and private sectors, fuel suppliers, labor unions, and others. The Group summarized major issues and posed options to be considered by EPA in developing a MACT rule.

Among the major issues raised, a couple remain with respect to the MACT alternative control plan: first, the presumptive three-year compliance period contained in §112(d) is too short. Based on real-world considerations, and particularly for those facilities that would be required to make major capital expenditures (e.g., installing a scrubber), it will take many years to bring all coal-fired electric utility steam generating units into compliance with a MACT standard. Second, the extremely restrictive emission limits for new sources do not appear to be justified based on the rationale for the emission limits for existing units.

Although the MACT alternative allows for some flexibility for power plants to achieve those reductions—subcategorization by coal type, accounting for variability in emissions and plant operations in the MACT floors, a 12-month rolling average to measure compliance, allowing facility-wide averaging, the format of the standard for existing units—analyses by the U.S. Energy Information Administration (EIA)⁸ and others indicate that a command-and-control reduction program would be significantly more expensive than a cap-and-trade system that would achieve the same levels of mercury emission reductions.

Cap-and-Trade Alternative Control Plan

Emissions trading is a system of establishing a cap on emissions and allowing sources the flexibility to choose the emissions reduction plan that works best for their situation, including increasing efficiency, using lower-emitting fuels, installing pollution control equipment, and trading. Trading allows a source that can over-control its emissions to sell extra reductions to another source for which controls would be very expensive or technologically difficult (e.g., small units). Without trading, small units may have to shut down, even though their total emissions are low. Emissions trading gained prominence with the implementation of the Title IV (Acid Rain Control) trading program for SO₂ in the 1990 CAAA.

The other alternative control plan in the Utility Mercury Reductions proposal is a market-based cap-and-trade approach. The proposal would amend CAA §111 rules and would establish a mechanism by which mercury emissions from new and existing coal-based power plants would be capped at specified, nation-wide levels. EPA states that the primary goal of this approach is to reduce power plant mercury emissions 70 percent from current levels by 2018, and

sets a 15 ton cap on these emissions in 2018. A near-term cap is also set in 2010 at a level that reflects mercury “co-benefits”—defined as the maximum reduction in mercury emissions that could be achieved through the installation of FGD and SCR units that will be necessary to meet the 2010 caps for SO₂ and NO_x in the proposed IAQR.

Some critics view emissions trading as “buying the right to pollute,” expressing concern about local “hot spots” where emissions could increase as a result of emissions trading. Many groups accept this logic for mercury and oppose mercury trading due to perceived “localized effects on public health.” Based on many years of real-world experience, studies of the SO₂ allowance trading program conducted by EPA,⁹ the Environmental Law Institute,¹⁰ and Resources for the Future¹¹ demonstrate that trading did not significantly change where emission reductions actually occurred. The clear success of the acid rain SO₂ trading program provides evidence to allay fears about localized effects.

There are two major reasons which suggest that localized effects will not occur with a mercury emissions trading program. One, the trading of allowances is most likely to involve large coal-based power plants controlling their emissions more than required and selling allowances to smaller plants. This viable assumption is based on the basic economics of capital investment in the utility industry. Under a trading system where emission-removal effectiveness is unrelated to plant size, it makes more economic sense for the utility to allocate pollution-prevention capital to its larger facilities than to smaller plants (since more allowances will be earned). Thus, any economies of scale of pollution control investment will favor investment at the larger plants. Two, the species of mercury that are deposited locally—oxidized and particulate mercury—are controlled by the same equipment that controls fine particles, SO₂ and NO_x. As noted earlier, these species of mercury are more likely to be deposited locally than gaseous elemental mercury, which is transported long distances from the source. As utilities install controls to comply with the new fine particle and ozone control regulations of the IAQR, a “co-benefit” in mercury control will accrue as particulate controls, scrubbers, and SCR units are installed on an increasing percentage of coal-based power plants. Therefore, the economics of a trading system are likely to favor controls of mercury that are likely to be deposited locally, thereby reducing any local hot spots.

Legislative Multi-Emissions Approach.

Many in government, industry, and academia believe that the current regulatory approach—with its uncoordinated and inconsistent air quality regulations—is duplicative, costly, and complex, and presents significant challenges and uncertainties. Coal-based electric generators are currently subject to more than 20 major environmental regulations aimed at reducing power plant air emissions. For these reasons, many policymakers and regulators have concluded that there is a better way to achieve air quality goals, while protecting the environment and public health. A “multi-emissions” strategy, if properly designed, could streamline the current regulatory process, provide greater certainty to electric companies, accomplish the nation’s air quality goals at a fraction of the cost, and maintain a reliable supply of electricity.

The National Energy Policy report released in May 2001¹² noted that uncertainty about future environmental controls is of particular concern for companies that operate existing coal-based power plants, and that future coal electricity generation will need to meet new challenges to reduce mercury emissions. To address these concerns, the report recommended that EPA work with Congress to propose legislation that would establish a flexible, market-based program to reduce and cap emissions of SO₂, NO_x, and mercury from electric

power generators. The report concluded that such a program would provide significant public health benefits even as electricity supplies are increased.

As a result of the report's recommendations, numerous proposals have surfaced to reduce utility mercury emissions. These range from applying "co-benefits," to 90 percent-plus removal. In February 2003, the "Clear Skies Act of 2003" was introduced, which requires sulfur dioxide (SO₂), nitrogen oxides (NO_x), and mercury emissions from power plants to be reduced by about 70 percent over the next decade using a market-based cap-and-trade approach.

A legislative strategy for improving air quality—with clear, congressionally-mandated emissions cuts—would provide far greater certainty and produce air quality improvements almost immediately. The Utility Mercury Reductions proposal's cap-and-trade alternative approximates the requirements of the Clear Skies Act, but ultimately leaves the design of the program up to individual states. This could be potentially confusing to implement and prove more costly to electricity customers than a national cap-and-trade program, which would reduce emissions just as fast. The MACT alternative would be far more expensive—yet no more effective—than a cap-and-trade approach. EPA Administrator Mike Leavitt, in announcing the Utility Mercury Reductions proposal, said it best himself: "Enacting Clear Skies is by far the best route to better air quality in the most cost-effective manner."

Conclusion

Federal efforts to limit electric utility mercury emissions continues to proceed on two tracks. In the Utility Mercury Reductions proposal, EPA has recognized that scientifically justified and verifiable mercury reductions can be achieved while at the same time providing the electric utility industry some flexibility to achieve those reductions. Further, EPA acknowledges that this flexibility can be achieved by subcategorization based on coal type, and by taking into account plant operational variability over time in setting the emission limits. However, allowing for market-based mechanisms such as trading will help achieve overall reductions and further increase the cost-effectiveness of any program.

The scientific data underlying these policy options to reduce utility mercury emissions is still evolving. EPA recognized this in its explanation of the agency's proposal to revise the regulatory finding that it made on December 20, 2000. The electric utility industry continues to test the effectiveness of various pollution control systems in reducing mercury emissions, and is funding additional health effects, fate-and-transport, and other related research. Accordingly, electric utilities are committed to working with DOE and EPA to address concerns with respect to the efficacy of emerging, mercury-specific control technologies, which are relatively new and untested on a commercial scale.

The electric power industry is subject to a broad array of federal, state, and local statutes and regulations, and is one of the nation's most regulated industries. Electric companies have exceeded many statutory and regulatory emission reduction targets, despite a growing national demand for electricity and increased electricity production. The electric utility industry understands the importance of continuing to work with EPA as the regulatory process proceeds to the next step of promulgating a final rule.

As federal efforts continue, the industry will work to ensure that critical data on the effectiveness of various pollution control systems, as well as health effects and other important related research, are available to assist EPA in developing a mercury emissions reduction program that is protective of public health, scientifically sound, flexible, and cost-effective.

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ASSESSING THE IMPACTS OF LOCAL DEPOSITION OF MERCURY ASSOCIATED WITH COAL-FIRED POWER PLANTS

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Introduction

Mercury emissions from coal fired plants will be limited by regulations enforced by the Environmental Protection Agency. However, there is still debate over whether the limits should be on a plant specific basis or a nationwide basis. The nationwide basis allows a Cap and Trade program similar to that for other air pollutants. Therefore, a major issue is the magnitude and extent of local deposition.

Computer modeling suggests that increased local deposition will occur on a local (2 to 10 Km) to regional scale (20 to 50 Km) with the increase being a small percentage of background deposition on the regional scale.^{1,2} The amount of deposition depends upon many factors including emission rate, chemical form of mercury emitted (with reactive gaseous mercury depositing more readily than elemental mercury), other emission characteristics (stack height, exhaust temperature, etc), and meteorological conditions. Modeling suggests that wet deposition will lead to the highest deposition rates and that these will occur locally. Dry deposition is also predicted to deposit approximately the same amount of mass as wet deposition, but over a much greater area.² Therefore, dry deposition rates will contribute a fraction of total deposition on the regional scale.

The models have a number of assumptions pertaining to deposition parameters and there is uncertainty in the predicted deposition rates. A key assumption in the models is that the mixture of reactive gaseous mercury (RGM) to elemental mercury Hg(0) is constant in the exhaust plume. Recent work suggests that RGM converts to Hg(0) quickly. Deposition measurements around coal-fired power plants would help reduce the uncertainties in the models.

A few studies have been performed to examine the deposition of mercury around point sources. Measurement of soil mercury downwind from chlor-alkali plants has shown increased deposition within a few Km.³ Studies of soils, sediments, and wet deposition around coal plants typically find some evidence of enhanced deposition; however, the statistical significance of the results is generally weak. A review of these studies is found in Lipfert.⁴

This study combines modeling of mercury deposition patterns with soil mercury measurements. The model used emissions data, meteorological conditions, and plant data to define sample locations likely to exhibit deposition in excess of background, that can be attributed to the power plant. Data were collected at the specified locations in November, 2003.

Deposition Modeling

In this attempt to validate the modeled enhanced deposition of Hg around coal-fired power plants, a field study was conducted around a large coal-fired power plant in the Midwest. The plant typically emits several hundred pounds of mercury per year. Meteorological data for a five year period were reviewed to

determine wind patterns under dry and wet conditions. Under dry conditions, the prevailing winds ran along an axis from the northwest towards the southeast. Winds occurred regularly in each direction along the axis. Under wet conditions, winds were generally from the north and east. This leads to predictions of wet deposition near the plant and to the southwest. Deposition modeling based on the meteorological data predicted highest deposition rates within 10 Km of the plant in a southwesterly direction, Figure 1. Dry deposition rates were lower than wet deposition rates and were not predicted to be a major contributor to deposition in the region. This analysis was used to select appropriate sample locations in the vicinity of the plant.

Experimental

Soil Samples. Soil samples were collected at 54 selected sites around the coal-fired power station as shown in Figure 1. At each site, five samples were collected. Three surface samples from the top five centimeters of soil separated by approximately 3 m, one deep sample at a depth of 5 – 10 cm, and one sample of the vegetation. The general layout of sample locations suggested by the modeling was modified to account for site-specific conditions (e.g., inaccessibility of sample locations, site activities, and changes in soil type which would alter background levels of mercury). The sampling area south and west of the plant covered an approximately square region of 64 km². The land surrounding the power plant was either part of an active strip mine or agricultural. Although many sampling sites were within the strip mine permit area, most of the land had been reclaimed. Strip mine personnel identified sites that had been fully reclaimed, or were at least known not to have been disturbed for at least a year. Agricultural area sampling sites were chosen because they appeared undisturbed for at least one year (i.e. had not been plowed). Many of the agricultural sites were at the crest of roadside ditches, adjacent to a plowed or mowed area.

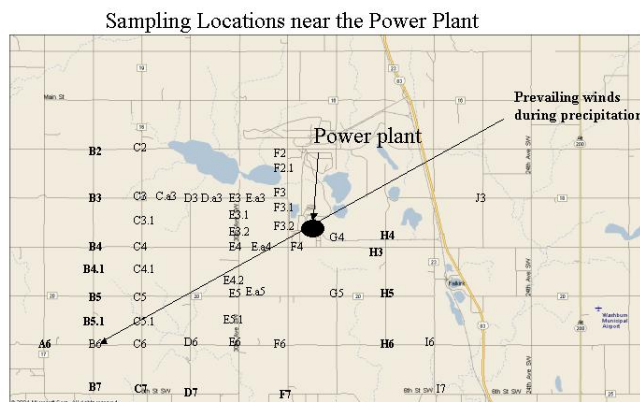


Figure 1. Soil Sample locations around the power plant.

Samples of approximate 100 grams weight were collected in water-tight wide-mouth 250 mL plastic screw-top cups. Samples were collected using stainless steel trowels, which were rinsed with tap water and wiped dry between each use. Blind field duplicates were collected every 10th sample. Latitude and longitude for each sample location were identified using a GPS locator system (Garmin Etrex) with a resolution of 6 meters.

Mercury Analysis Methods. The soil samples were shipped back to Brookhaven National Laboratory for analysis using a Direct Mercury Analyzer (DMA-80, Milestone, Inc, Monroe, CT). In the DMA-80, controlled heating in an oxygenated decomposition furnace liberates mercury from the solid samples. Flowing oxygen to the catalytic section of the furnace carries the decomposition products, where oxidation is completed and halogens and nitrogen/sulfur oxides are trapped. The remaining decomposition products are then carried to a gold amalgamator that selectively traps mercury. After the system is flushed, the amalgamator is rapidly heated, releasing mercury vapor, which is then carried through absorbance cells positioned in the light path of a single wavelength (253.7 nm) atomic absorption spectrophotometer. The typical working range for this method is 0.05-600 ng of mercury. Since soil samples are at most about 0.5 grams, the DMA-80 easily measures levels below 1 ppb (ng/g).

DMA-80 analyses were conducted on soil samples as is. Moisture content was determined separately for all samples, and mercury concentrations were adjusted to a dry weight basis.

Quality assurance was evaluated through taking blind duplicates of 10% of the samples, measurement of empty sample boats in the DMA-80, and use of two NIST mercury soil standards (SRM 2709 and SRM 2710) at every 10th measurement. Soil samples will be counted in triplicate to examine for heterogeneity of the samples.

Results and Discussion

Sample analysis is underway and all of the soil locations have been analyzed for mercury, on as received (wet) basis at least once. At each sample location, the three surface soil samples were averaged to give a composite. Typically, the three adjacent surface samples from any site had agreement in the mercury levels to within 10%. At the fifty-four locations the average value was 21.5 ng/g (wet weight basis), with a standard deviation of 5.7. The minimum value was 8.9 ng/g and the maximum value was 43 ng/g.

Comparison between the predicted deposition versus measured mercury concentrations in the soil was accomplished by placing the deposition map over the sampling map coded to measured concentration. Areas of increased deposition are anticipated to have increased soil mercury concentrations. Figure 2 is the graphical representation of the analysis. Predicted regions of enhanced deposition are covered by the dark filled contour. Sample locations with symbols representing measured mercury levels represent the measured data.

Examining Figure 2 shows that the modeled and measured data match reasonably well. The overall shape of the region of excess deposition matches, however, the measured data suggest that the main finger of the plume is slightly south of the area predicted by modeling. There is scatter in the data, as expected with an environmental data set. Statistical analyses will be performed to determine the degree of confidence in these results. The results presented are preliminary and will be refined after completion of the analysis of all soil and vegetative samples.

Although there is evidence of excess deposition near the plant, mass balance calculations comparing emissions with increased soil levels of mercury indicate that less than 5% of emissions are deposited over the sampling domain.

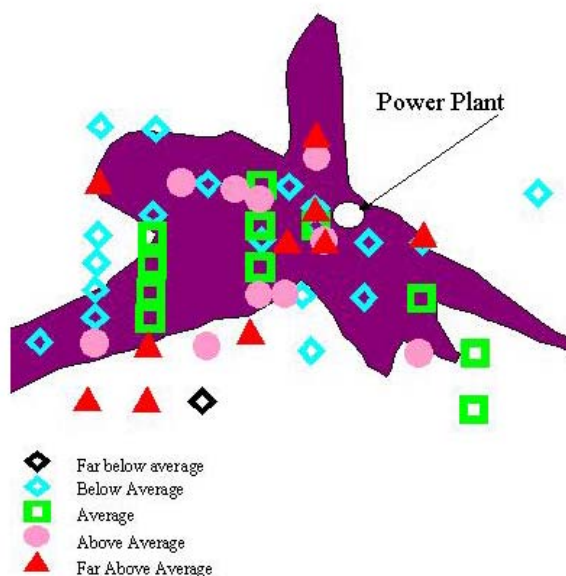


Figure 2. Comparison of modeled deposition pattern (solid contour) with measured data.

Acknowledgment

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ASSESSING THE MERCURY HEALTH RISKS ASSOCIATED WITH COAL-FIRED POWER PLANTS: ISSUES IN ATMOSPHERIC PROCESSES

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Introduction

The rationale for regulating air emissions of mercury from U.S. coal-fired power plants largely depends on mathematical dispersion modeling, including the atmospheric chemistry processes that affect the partitioning of Hg emissions into elemental (Hg_0) and the reactive (RGM) forms that may deposit more rapidly near sources. This paper considers and evaluates the empirical support for this paradigm. We consider the extant experimental data at three spatial scales: local (< 30 km), regional ($< \sim 300$ km), and national (multi-state data). An additional issue involves the finding of excess Hg levels in urban areas.

Local Evidence

Our search of the literature found seven studies dating back 30 years in which various manifestations of local Hg deposition were related to coal-fired power plants (Table 1). These experiments involved concentrations of Hg in soil, lake sediments, precipitation and fish. To place these results in a common framework, we estimated the relationships between background concentrations and those obtained near the plant and the fractions of emitted Hg that had been deposited and retained during the period of facility operation. Where possible, we accounted for these relationships as a function of the receptor's distance from the plant.

Soil Composition. The earliest attempts at assessing Hg impacts from coal-fired power plants were based on the Hg content of surficial soil samples¹⁻³. This technique is highly dependent upon definition of the background soil content, which was not always reliable. The reported incremental Hg concentrations ranged from 29%¹ to 42%² above background, corresponding to retention of 3-5% of cumulative emissions. The Four Corners study³ did not measure background but concluded that "mercury was not accumulating in the soil", based mainly on comparisons of local soil Hg concentrations with those reported in the literature for other locations. However, reanalysis of the published data on individual soil samples shows a significant overall (log-log) slope of -0.11 ($p < 0.005$) as a function of downwind distance. Moreover, scatter plots showed wide variation by wind direction, a more rapid decrease in soil Hg near the plant, and the suggestion of a secondary peak at about 10-15 km downwind. A possible rationale might thus be a close-in peak due to rainout and a more distant peak due to plume touchdown and dry deposition. We assumed various values of background Hg in order to estimate the fraction of emissions deposited and retained in the soil; the wide range of these estimates shows the sensitivity to this parameter. It appears that around 10% of the plant's Hg emissions may have been deposited and retained in the soil, which would correspond to excess deposition rates of about 60%. Such estimates are also sensitive to the maximum downwind distance considered, which was 20-30 km in these various examples.

Sediments. Three studies^{2,5,6} include data on the Hg content of sediment cores obtained from nearby water bodies. This technique has the advantage of potential relevance to impacts on fish but has the disadvantages of uncertain time periods and the difficulty of considering decay rates in terms of downwind distance. At the

Kincaid plant², the excess Hg in sediments was reported to be about 30%. In Texas⁶, there was about 18% more Hg in sediments from a lake near the plant than from two lakes about 30 km away. The decreases in Hg with depth within the core were also substantially larger in the sediment cores from the nearby lake.

Precipitation. Two studies^{5,7} considered variations in the Hg content of precipitation as a marker for local impact. In Slovenia⁵, it was not clear that valid annual averages had been obtained and no comparisons were made with local background. In Indiana⁷, the authors reported no significant difference between the precipitation Hg data collected near the power plant and that collected at 3 other sites in the state. However, precipitation chemistry is frequently sensitive to the rate and thus amount of precipitation, and when this factor is taken into account in a multiple regression analysis, the site near the plant appears to have an excess Hg level of about 12% (Figure 1). With normalized deposition (deposition/precipitation) as the dependent variable, the increment is just significant ($p < 0.03$).

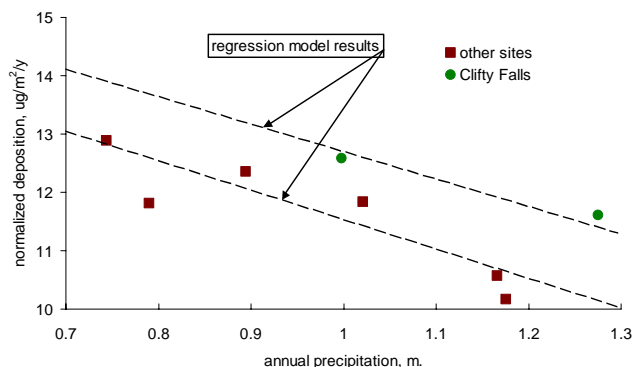


Figure 1. Comparison of wet deposition at Clifty Falls Mercury Deposition Network (MDN) monitoring site.

Fish Hg Content. Two studies^{2,4} reported the Hg content found in various species of fish collected in or near the impacts zones of power plants. At Kincaid², the fish caught near the plant had substantially less Hg than those from more distant locations, but it was not clear whether this comparison included adjustments for fish size. For each of the 23 farm ponds in the Dickerson study⁴, fish lengths and detailed water chemistry data were also reported, which turned out to be important. To examine these factors, we estimated wet deposition of Hg to each pond based on the modeled isopleth plots in the paper. In multiple regression analysis, the log of fish Hg content was significantly ($p < 0.01$) associated with the log of wet Hg deposition (coefficient = 0.5), pond water conductivity (coefficient = -0.5), and fish length for sunfish and bass pooled ($n=37$). Fish length was essentially a surrogate for fish species. Water conductivity, hardness, and alkalinity were highly inter-correlated; pH was not a significant predictor of fish Hg. Water quality was not associated with estimated Hg wet deposition. Figure 2 is scatter plot of these data, based on fish Hg adjusted to a common level of pond water conductivity. Note that only one sample clearly exceeds the EPA guideline for fish Hg content (0.3 ppm), notwithstanding the effects of the power plant; 3 samples exceeded this level in the unadjusted data.

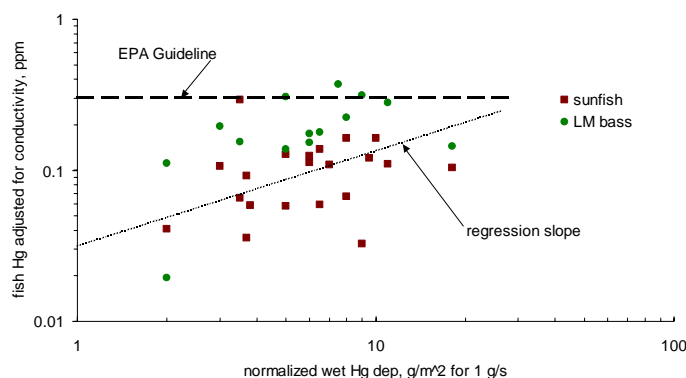


Figure 2. Comparison of measured fish Hg (ppm) as a function of predicted wet deposition.

Regional Data

As an example of regional relationships, we used data on Hg emissions from power plants⁸ and on 1998-2002 wet Hg deposition obtained from the Mercury Deposition Network (MDN)⁹, both for Pennsylvania. The 8 MDN stations operated for various portions of this period; each annual wet deposition estimate was thus treated as a separate observation ($n=22$). The straight-line distance between each MDN site and each of the 36 plants, whose Hg emissions ranged from 637 kg to 45 g, totaling 3622 kg, was computed from latitude-longitude data, and each emission rate was weighted by the inverse square of this distance and summed. For the 8 MDN sites, these sums ranged from 0.09 kg/km² to 1.7 kg/km².

Multiple regression analysis was then used to deduce source-receptor relationships, considering the year, site elevation, and site latitude as possible confounders. No account was taken of other point sources of Hg (such as urban areas or out-of-state sources) or of prevailing wind directions for precipitation events. MDN site latitude was included as a possible confounder because the national map of Hg wet deposition seems to show consistent increases from north to south in the eastern states.

The coefficients for site elevation and year were far from significant and were dropped from further consideration. Latitude and (emissions/distance²) were moderately (negatively) correlated, which posed a co-linearity problem. However the best fit to these 22 observations was obtained in a log-log regression based on the emission parameter alone, which had a log-log coefficient of 0.11 ($p<0.010$). This result implies that 11% of the wet Hg deposition in Pennsylvania is associated with coal-fired power plants in the state, under the modeling assumptions stated above. It also implies that wet deposition of Hg may decrease more slowly with downwind deposition than originally assumed. However, when various assumed levels of background wet deposition are subtracted from the measured MDN values, the regression coefficients are increased, at the expense of poorer model fits.

As an example, this empirical model would predict the following annual deposition ($\mu\text{g}/\text{m}^2$)-distance relationship for an isolated point source of 636 kg Hg per year: 1 km., 19.5; 3 km, 15.3; 10 km, 11.7; 30 km, 9.2; 100 km, 7.1. Taking the last figure as "background", the annual wet deposition would be about 1.1% of emissions and the total Hg deposition, about 2.2%.

Additional information on Hg deposition at the regional scale is provided by the results of Lopez-Alonzo et al.¹⁰, who analyzed the Hg content of calf kidneys in relation to distances between the farms and major point sources of Hg in Northwest Spain. (e.g. 1200 kg/y from coal-fired power plants and similar amounts from other

industries). Downwind distances ranged up to 140-200 km; the duration of this deposition was not mentioned. Based on approximations from the scatter-plots¹⁰, it appears that deposition decreased with downwind distance to the 0.4 power for the power plants and 0.7 power for the industrial area. Neither of these slopes is significantly different from the expected square-root relationship.

The National Scale

We used state-level data on Hg deposition (MDN) and fish Hg concentrations¹¹ to deduce larger scale source-receptor relationships. The deposition data were averaged over time (1997-2002) and the fish Hg data were considered by species (9 different species). A simple regression model was used in which $\ln(\text{fish Hg})$ was regressed against $\ln(\text{deposition})$ and dummy variables for fish species. This model assumes that all species react to deposition in the same way and provides fish Hg concentration increments relative to a referent species, in this case large-mouth bass. This approach provided 105 combinations of states and fish species (only 31 states were represented). Channel catfish, bluegills, common carp, white suckers, and yellow perch all had significantly lower Hg concentrations than bass, walleye, or northern pike (as expected). However, the effect of Hg deposition, as averaged over entire states, was significantly negative in this model ($p < 0.025$). Latitude was not an important confounder when both eastern and western states were considered. When large-mouth bass were considered alone ($n=20$), the relationship with deposition was positive but far from significance (log-log coefficient = 0.21).

A further consideration at the national scale is provided by the recent global modeling study of Seigneur et al.¹², who estimated that 25-32% of the total Hg deposition to the contiguous US came from North American anthropogenic sources. These sources total 200.1 metric tons/y, of which electric utilities comprise 52.7 tons, or 26.3%. Assuming proportionality, the utility share of deposition would then be about 6.6-8.4%, which is in line with the various estimates above that are based on actual measurements. Comparison of these figures suggests a minor role for Hg deposition at distances $> \sim 100$ km.

Discussion

The above findings lead to the overall conclusion that atmospheric deposition of Hg is affected by emissions from coal-fired power plants. However, because of the numerous assumptions required and the use of simplistic models, it is not possible to accurately describe these relationships on this basis. Complex atmospheric chemistry and dispersion models are required to predict precise concentration and deposition contributions, and aquatic process models are required to predict effects on fish.

These caveats notwithstanding, it is still useful to summarize the consistencies and inconsistencies in our findings. In terms of excesses over background, we see local soil concentration Hg increments of 30%-60%, sediment increments of 18-30%, and wet deposition increments of 11-12%. If we accept the finding⁷ that fish Hg is proportional to the square root of wet deposition (after controlling for water chemistry), then the contribution of coal-fired power plants to fish Hg would be about 5-6%. It is possible that the absence of local impacts on fish at Kincaid was due to water chemistry. Local differences in water chemistry may also help explain the absence of a relationship between state-level fish concentrations and wet deposition levels.

Effects on public health should be less than a few percent as more than 90% of the population currently meets the EPA exposure guideline and few individuals consume large quantities of fresh-water fish where coal is burned.

Finally, it should be noted that none of these simple analyses have accounted for possible impacts from urban areas, as implied by recent findings of excess urban deposition.^{13,14} A mass-balance study of Hg deposition to Lake Michigan¹⁵ showed a slow rate of decrease in deposition (in terms of distance from Chicago), as did the data on power plants discussed above.

Given the resources required to control mercury from power plants, a comprehensive campaign to measure their mercury impacts in detail and to monitor any ensuing changes would be prudent.

Acknowledgment

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Table 1 Local Hg deposition from coal-fired power plants

reference	plant data	emissions	deposition data, ppb in soils, ug/m ² /yr in precip			percent		remarks
		kg/y	type	# samples	mean	background	deposited	
Klein & Russell (1973)	Campbell, MI (?) 650 MW 122 m stack	~290	soil	90	10.2	7.9	2.7	irregular impact area
Anderson & Smith (1977)	Kincaid (IL) 1200 MW 2 152 m stacks	531	soil	90	22	15.5	4.6	limited to 1 sector of the impact area ~1% of emissions deposited in lake fish near plant unaffected
			sediment	36	49	37		
			fish	120	70-82	110-560		
Crockett & Kinnison (1979)	Four Corners (NM) 2150 MW 2 76, 2 91 m stacks	595	soil	70	14.5	*0	20.6	*assumed background values
						*3	16.3	
						*6	12.0	
						*9	7.8	
Pinkney et al. (1997)	Dickerson (MD) 543 MW	~240	fish	69 sunfish 42 LM bass				fish Hg in 23 small farm ponds increased with (Hg dep) ^{0.5}
Kotnik et al. (2000)	Sostanj, Slovenia 775 MW 100, 150, 230 m stacks	314	precip lake sediments		7.4-13.7 ug/m ² 53-166		5	based on 20 km radius and dry dep = wet higher values in surface layers
Menounou & Presley (2003)	Gibbons Cr (TX) 460 MW	~430	lake sediments	13 (cores)	94 (data from top layers)	80	30	based on 25 km radius and median excess deposit of 0.094 ug/cm ²
Risch (2003)	Clifty Cr (IN) 1300 MW	184	precip	4 sites, 2 yrs	12.3	11		ug/m ² /y at 110 cm precip (monitor 3 km from plant) Other plants in Ohio and Kentucky not considered

EVALUATION OF COAL COMBUSTION BY-PRODUCT MERCURY RERELEASE POTENTIAL

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Introduction

Mercury, known to be present in coal combustion by-products (CCBs) including primarily fly ash and flue gas desulfurization (FGD) materials, presents a potential environmental problem depending on the stability of the mercury under a variety of reuse or disposal conditions. The U.S. Environmental Protection Agency (EPA) announced on December 14, 2000, that it would regulate Hg emissions from coal- and oil-fired electric utility steam-generating power plants. EPA plans to issue final regulation by December 2004 and is expected to require compliance by December 2007.¹ As technologies are developed to reduce the air emissions of Hg, the amount of Hg in CCBs will likely increase. Recent studies have indicated that from 0% to 70% of the Hg originally in the coal can be associated with the fly ash.^{2,3}

The Energy & Environmental Research Center (EERC) has investigated the potential for the rerelease of Hg from CCBs under a variety of conditions in an effort to address various ash management scenarios. Four conditions that have been examined are leaching, long-term ambient-temperature vapor release, microbiologically mediated vapor release, and high-temperature thermal release.^{4,5} Leaching of CCBs has been ongoing at the EERC for over 25 years and vapor and thermal release methods have been investigated for the last several years.

Leaching is the most likely mechanism of transport of constituents from disposed or utilized CCBs contacted by water. Leaching is typically performed on CCBs to characterize them for management purposes. Recently, EPA proposed a leaching method for evaluating CCBs based on its interest in CCBs that may be affected by Hg emission controls. These recommendations do not adequately address some typical long-term behaviors of reactive alkaline CCBs under hydration conditions.

Thermal release, particularly of Hg, is important for long-term utilization, storage, and disposal of CCBs. Although the concentration of Hg in CCBs is relatively low, the large volumes of CCBs produced annually cause concern about potential Hg release. Ambient, near-ambient, and elevated-temperature studies of Hg release have resulted in the development of apparatuses to determine Hg release from CCBs. Vapor transport experiments evaluate Hg release from a bed of CCBs at ambient and near-ambient temperatures with constant airflow through the bed. The design of these and future experiments is critical to produce laboratory results that can be compared to field experiments at CCB management sites.

The wide distribution and variety of microorganisms in the environment indicate that microbiological Hg release needs to be investigated. A wide variety of specific microbe interactions can affect key elements associated with CCBs, including oxidation–reduction and alkylation–dealkylation reactions. In order for microbes to be metabolically active, a few constraints must be satisfied. In some CCB management options, these criteria are unlikely to be met, but for options where they can be met, laboratory experiments will simulate appropriate scenarios.

Experimental

Work is ongoing at the EERC to examine the rerelease of Hg from CCBs under four conditions including leaching, long-term ambient-temperature vapor release, microbiologically mediated vapor release, and high-temperature thermal release up to 700°C. CCBs with atypically high levels of total Hg content were selected as having a significant potential for releasing measurable amounts of Hg vapor for use in the long-term ambient-temperature and microbiologically mediated vapor-release experiments.

Leaching. Leaching of CCBs using various batch laboratory methods has been ongoing at the EERC for over 27 years. It became apparent early in EERC work that the methods being advocated and used were generating scientifically invalid and often misleading data. The EERC identified the inappropriate use of acetic acid in leaching solutions for CCBs understanding that CCBs would be unlikely to contact acetic acid under typical management conditions. Agreement by numerous research groups and government agencies that the use of acetic acid-based leaching solution is not appropriate for CCBs has led to many questions regarding what leaching methods are appropriate. Work at the EERC identified formation of secondary hydrated phases in alkaline CCBs, and it was determined that formation of these hydrated phases had a demonstrated influence on concentrations of certain trace elements in leachate. As a result of these observations, the EERC developed the SGLP (synthetic groundwater leaching procedure), including long-term leaching (LTL), to address discrepancies with existing methods.⁶

The SGLP batch-leaching procedure is a relatively simple test that follows many of the conditions of the toxicity characteristic leaching procedure (TCLP), EPA Method 1311.⁷ The test utilizes a 20:1 liquid-to-solid ratio, end-over-end agitation at approximately 30 rpm, and usually employs a leaching solution consisting of water from the site, water that has been prepared in the lab similar to water likely to contact the ash, or distilled deionized water. For the long-term component of this procedure, multiple bottles are set up and analyzed at different time intervals. A typical SGLP and LTL test might consist of 18-hour, 30-day, and 60-day equilibration times. Although 60 days is often not long enough to have achieved complete equilibrium, it is generally long enough to determine the concentration evolution of individual parameters. The most important factor when performing LTL is to have at least three equilibration times to determine a true trend.

The majority of the leachate data on file was generated using leaching procedures with a 20:1 liquid-to-solid ratio with a few 4:1 liquid-to-solid ratio leachings. The 20:1 liquid-to-solid ratio leaching procedures included SGLP, LTL with 30- and 60-day equilibration times, TCLP, synthetic acid leaching (SAL), and synthetic precipitation leaching procedure (SPLP).⁸ Distilled deionized water leachings were completed with 18-hour, 2-week, and 4-week equilibration times using a 4:1 liquid-to-solid ratio.

A wide variety of CCBs have been leached at the EERC. Sample types have included atmospheric fluidized-bed combustion (AFBC) char fly ash, AFBC spent bed material, boiler slag, bottom ash, circulating FBC fly ash and bottom ash, coal fines, FBC bottom ash, FBC fly ash, FGD material, and FGD–fly ash mixtures, fly ash, fly ash with Hg sorbent material, and particulate test combustor (PTC) fly ash.

Long-Term Ambient-Temperature Vapor Release. Long-term vapor release of Hg has been investigated utilizing six CCB samples obtained from members of the Coal Ash Resources Research Consortium⁹ (CARRC⁹). The ashes selected included two eastern bituminous fly ashes, two South African fly ashes, one Powder River Basin (PRB)–pet coke fly ash, and one PRB FGD material.

A 150-gram aliquot of ash was placed and compacted into 250-mL tall wide-mouth bottles with a bonded Teflon liner cap. The cap was drilled with two holes to accommodate a Teflon outlet bulkhead fitting and a silicone tube for gas inlet (see Figure 1). Two samples of each CCB were set up for duplicate analyses. Breathing-quality air from a cylinder was passed through several sets of gold-coated quartz traps for Hg removal and admitted to each of the bottles through a gas distribution manifold that routed the gas through 0.23-mm gas chromatography (GC) capillary tubing to each of the individual bottles. The pressure drop across the GC capillary tubing allowed for the regulation of air flow through each bottle by simply adjusting the length of tubing to each bottle. The length of tubing was a nominal 65 cm using GC tubing with an ID of 0.25 mm. This length of tubing, when pressurized to between 1 and 2 psig through a gas distribution manifold, provided a convenient means of regulating gas flow to approximately 2 cm³/min. Because of the variability of particle sizes between different ash samples, the sample with the initial highest gas flow was left with a 65-cm length of GC tubing and other samples had their tubing lengths shortened until all samples had approximately the same flow rate. The air exiting the GC tubing was given a final scrubbing to remove Hg vapor using gold-coated quartz just prior to entering the bottle containing the CCB. After entering the bottle, the air passed through the ash and exited to a central Hg collection tube containing two separate gold-coated quartz traps. The gold-coated quartz nearest the exit bulkhead fitting was analyzed at regular intervals to determine the mass of Hg vapor released from the CCBs while the top trap, in the same tube, was present to prevent Hg contamination from atmospheric Hg. This setup is clearly illustrated in Figure 1.

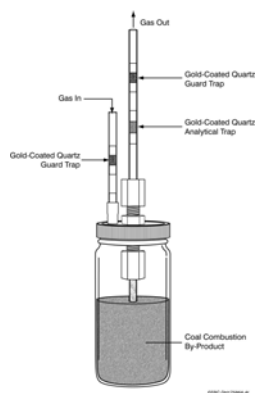


Figure 1. Long-term Hg-vapor release collection apparatus.

The gold-coated quartz collection tubes were desorbed for analysis by heating to approximately 500°C, and the mass of Hg released was determined using atomic fluorescence. The tubes were desorbed several times with varying periods of collection over the length of the experiments. Following the collection of Hg from the CCBs in Test 2, blank values were determined for each separate bottle by emptying the bottles of ash and flowing gas through the empty bottles for two 90-day periods. The gold-coated quartz tubes were analyzed for Hg as described above.

Microbiologically Mediated Vapor Release. Four CCBs have been examined for the microbiologically mediated vapor release of Hg. The tested CCBs have included a neutralized subbituminous FGD material, a hydrated subbituminous fly ash, and two eastern bituminous fly ashes.

The apparatus used for this testing has been improved numerous times over the course of the research; therefore, only the latest setup will be described here. A 250-mL Erlenmeyer flask fitted with an

impinger inlet/outlet tube with the inlet center shortened to 6 cm below the standard taper. Gas inlet flow was regulated in the same manner as in the long-term Hg vapor release experiments described above; however, all GC capillary tubing was approximately 60 cm in length. The Hg vapor-collection system differed from the long-term ambient-temperature setup, consisting of two traps. The nearest trap contained Supelco Carbotrap, which collected organomercury compounds. This was followed by a gold-coated quartz trap, which collected Hg⁰.

The flasks were placed on a 16-flask wrist-action shaker. The experimental matrix consisted of eight flasks under aerobic conditions (using breathing-quality air) and eight flasks under anaerobic conditions (using argon). In each set of eight flasks, two contained only buffer, three contained the CCB with buffer, and three contained the CCB with buffer and glucose. An 80-gram aliquot of CCB was placed in the flasks and 100 mL of a phosphate buffer (with or without glucose) was added to create a neutral pH. The ash-containing flasks also had 100 µL of mixed bacterial culture added. The source of bacteria was a mixed bacterial inoculum from a brackish wetland. This apparatus is shown in Figure 2.



Figure 2. Microbiologically mediated Hg vapor-phase collection apparatus.

The experiments were conducted for 30 days. The total mercury collected on the carbon traps was determined. The gold-coated quartz collection tubes were desorbed for analysis by heating to approximately 500°C, and the mass of Hg released was determined using atomic fluorescence. For bacterial counts at the completion of the 30-day period, a 1-mL aliquot of solution was taken from each flask. The aqueous supernate was serially diluted in 0.1% sodium pyrophosphate buffer (pH 7.0) and then used to inoculate a series of tubes containing 1% peptone, tryptone, yeast extract, and glucose broth. The tubes were incubated at 30°C, and growth, as turbidity, was monitored over a 3-week period.

High-Temperature Thermal Release. A schematic for the controlled thermal desorption of Hg and Hg compounds was assembled and is shown schematically in Figure 3. The apparatus was constructed using an atomic absorption (AA) spectrophotometer for Hg detection and included a small tube furnace and temperature controller for thermal desorption. A Hewlett Packard 3395 integrator was used for data collection. Detection of thermally desorbed Hg and Hg compounds was done in an electrically heated quartz cell operated at 800°C. The use of a heated cell allowed detection of Hg compounds by thermally decomposing compounds to form Hg⁰, which can be detected by AA. Gas flow was 20 cm³/min of nitrogen. The temperature controller was ramped from ambient temperature to

700°C at a rate of 25°C per minute. A more complete description along with a description of the experimental protocol can be found elsewhere.⁹

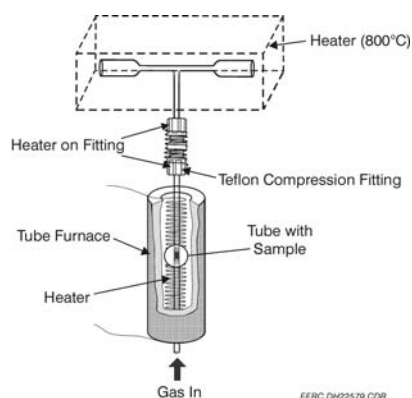


Figure 3. Hg thermal desorption apparatus.

Results and Discussion

An overview of some of the results obtained from the various Hg release techniques is included below.

Leaching. Over the last nearly 28 years, researchers at the EERC have leached a large number of varying CCBs, initially using the more common standard tests.

Data from the past ten years contain 256 Hg leachate values. Only 32 of those values (12%) had detectable Hg values, ranging from 0.01 to 0.39 µg/L. The average is 0.064 µg/L, and the median is 0.02 µg/L. Hg values above the detection limit were obtained in all procedures used except SAL, SPLP, and the 4:1 liquid-to-solid ratio 4-week distilled deionized water. Detectable Hg leachate values resulted from AFBC char fly ash, AFBC spent bed material, boiler slag, bottom ash, fly ash, fly ash with Hg sorbent material, and PTC fly ash.

A total of 38 Hg leaching data points of fly ash resulting from the use of full-scale Hg control technologies are in the current data set. Eleven of the data points are at or above the detection limit of 0.01 µg/L used on those samples.

Long-Term Ambient-Temperature Vapor Release. To date, two complete sets of long-term release experiments have been completed on six CCBs. Tests 1 and 2 were conducted for 263 and 264 days, respectively. The averaged duplicate results from Test 2 are shown in Table 1. It is apparent that all but one of the ash samples appear to be sorbing Hg. The total Hg contents of the ashes had a range of 0.112–0.736 µg/g.

Table 1. Comparison of Emission Rates Between the Empty Bottles and the Bottles Containing Ash in Test 2, pg/day

Sample	Bottles with Ash	Bottles without Ash	Difference
99-188	2.237	2.161	0.076
99-189	0.077	1.127	!1.050
99-692	0.081	2.454	!2.373
99-693	0.077	4.328	!4.251
99-722	0.696	7.165	!6.469
99-724	0.411	4.436	!4.025

Microbiologically Mediated Vapor Release. Two CCB samples with various electron acceptors added were analyzed in the first microbiologically mediated Hg vapor-release experiment. Results from this test were very confusing with the sterile sample

releasing the most Hg. It was decided that the CCB would suffice as a source of the various electron acceptors.

Testing of three CCBs has been completed using the matrix described in the experimental section, including one of the fly ash samples from the first experiment. Results have been confusing; however, general trends have emerged. The Hg released from the CCB slurry was generally higher in the samples fed with glucose versus starved samples and in aerobic versus anaerobic conditions. The bacterial count has also generally followed that trend. The Hg⁰ vapor captured on the gold-coated quartz traps has been higher than seen in the long-term ambient-temperature vapor-release experiments. The flasks containing buffer only have been treated as blanks.^{5,10}

High-Temperature Thermal Release. A large variety of CCBs have been analyzed for the thermal release of Hg. Most of the thermal curves generated were straightforward, containing only one or two major desorption peaks.

Thermal desorption curves were rather difficult to interpret since there is no way, at present, using this apparatus to determine exactly what is happening during the thermal treatment. There are several possible scenarios:

- Hg and Hg compounds, as sorbed, are being released unchanged during the thermal desorption procedure.
- Hg compounds are being desorbed by a mechanism of thermal decomposition whereby sorbed compounds such as HgO are thermally decomposed to Hg and oxygen during the thermal desorption.
- Hg or Hg compounds are chemically reacting with the CCB components then thermally desorbed according to the first or second scenario as described above.

Conclusions

Currently, many CCBs contain relatively little Hg; however, in the future, as Hg emissions are controlled, Hg-containing sorbent in CCBs will likely cause Hg concentrations to increase. The issue of Hg emissions from disposed or utilized CCBs requires additional study.

A variety of CCBs have been leached using a variety of batch-leaching procedures. In the overall data set over the past 10 years, 12% of the leachate values were above the detection limit and 29% of the leachings from full-scale Hg control technology CCBs yielded detectable Hg values. That number of samples is low; therefore, the effect of Hg control technologies on the leachability of Hg from CCBs is yet to be seen.

Long-term ambient-temperature release experiments have indicated that five of six CCBs analyzed acted as Hg sinks, although these samples were previously reported as having released small amounts of Hg vapor.¹¹

The most likely species of Hg to be released in the absence of biological activity is elemental Hg because of its significant vapor pressure although other species are likely in CCBs at room temperature. All have extremely low vapor pressures and are unlikely to be released in significant amounts at ambient temperatures.

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Implications of Mercury Interactions With Band-Gap Semiconductor Oxides
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Abstract

Titanium dioxide is a well known photo-oxidation catalyst. It will oxidize mercury in the presence of ultraviolet light from the sun and oxygen and/or moisture to form mercuric oxide. Several companies manufacture self-cleaning windows. These windows have a transparent coating of titanium dioxide. The titanium dioxide is capable of destroying organic contaminants in air in the presence of ultraviolet light from the sun, thereby keeping the windows clean. The commercially available self-cleaning windows were used to sequester mercury from oxygen-nitrogen mixtures.

Samples of the self-cleaning glass were placed into specially designed photo-reactors in order to study the removal of elemental mercury from oxygen-nitrogen mixtures closely resembling air. The possibility of removing mercury from ambient air with a self-cleaning glass apparatus is examined. The intensity of 365-nm ultraviolet light was similar to the natural intensity from sunlight in the Pittsburgh region. Passive removal of mercury from the air may be less costly than point source clean-up at combustion facilities.

There are several common band-gap semiconductor oxide photocatalysts. Sunlight (both the ultraviolet and visible light components) and band-gap semiconductor particles can impact the global cycle of mercury in the environment. The potential environmental consequences of mercury interactions with band-gap semiconductor oxides are discussed. Heterogeneous photooxidation might impact the global transport of elemental mercury emanating from flue gases.

Introduction

Mercury is typically present in air at extraordinarily low concentrations of around 1 part per trillion by volume [1-15]. Mercury can exist in air in the elemental, oxidized, and particulate-bound forms. Between 97-99% of the mercury in air is believed to be in the elemental form [1-15]. Oxidized forms of mercury in the atmosphere are believed to include mercuric chloride and mercuric oxide [1-15]. The element and many of its compounds are powerful neurotoxins [16].

Mercury is a semi-noble metal, with a standard electrode potential for oxidation similar to palladium. This relative inertness allows elemental mercury emissions, once in the atmosphere, to transport across the globe. Elemental mercury is slowly oxidized in the atmosphere by ozone and hydroxyl radicals [8]. The low concentrations of elemental

mercury, ozone, and hydroxyl radicals contribute to the long residence time of elemental mercury in the air. Elemental mercury in the atmosphere has an estimated lifetime of approximately one year [8]. Elemental mercury is insoluble in water, whereas oxidized forms of mercury are typically much more soluble. Oxidized mercury is scrubbed from the atmosphere by precipitation and deposits in bodies of water. In oceans, lakes, rivers, streams, ponds, bogs, and marshes, oxidized mercury can be methylated by bacteria, plankton, and algae, thereby entering the food chain. Mercury can accumulate at the top of the food chain in large predator fish such as tuna, sword fish, and sharks. Consumption of certain species of fish has been of concern for pregnant women and young children. Numerous fish advisories have been recently posted in the United States [17].

Point source removal of mercury from coal-burning power plants is a difficult endeavor [16,18-23]. Mercury is present in flue gas at low concentrations of around 1 part per billion by volume [16]. The composition of a typical flue gas is given in Table 1. The use of activated carbon sorbent has been the most extensively examined method for removal of mercury from flue gas. There are many deficiencies in the use of activated carbon for mercury capture from power plant flue gas [16,18,19,21,23]. Carbon is a general adsorbent; it will adsorb many of the components of flue gas to some extent, with some in competition with mercury. Carbon sorbents work best at low temperatures. The final state of mercury on the spent carbon sorbent is a concern for the ultimate disposal or use of fly ash. Injection of activated carbon into the duct work of a power plant upstream of an electrostatic precipitator results in poor contact between the sorbent and flue gas. As a result of the poor contacting methods typically employed, a high carbon to mercury mass ratio of 3,000:1 to 50,000:1 is used to achieve a high level of mercury removal [16,18]. Activated carbons can be expensive, with a price of around \$500 - 3,000/ton [16,18]. Alternatives to activated carbon injection for point source removal of mercury have been developed both in-house at the National Energy Technology Laboratory and through contracted research funded by the United States Department of Energy [24-35].

The U.S. EPA has announced pending regulation of mercury emissions from U.S. power plants [36,37]. However, these regulations may not reduce the number of fish consumption advisories in the United States. U.S. coal-burning power plants are estimated to have stack emissions of 48 tons of mercury per year [32]. This is approximately 1% of the annual emissions of mercury around the globe from both anthropogenic and natural sources [32]. The growing unregulated emissions of mercury from Asian economies, as well as the global transport of elemental mercury emissions, suggest that other actions may be needed to slow or halt the accumulation of mercury in the food chain.

Passive removal of mercury from air may represent a better solution to the problem [38]. It is proposed that self-cleaning glass, a new and inexpensive product [39-41], could be an important component in the passive collection of mercury from the environment [38].

Self-cleaning glass is coated with titanium dioxide, a well-known photo-oxidation catalyst [39-41]. It can capture mercury from the air as mercuric oxide. The use of self-cleaning glass is envisioned in automobiles and buildings [38]. Mercuric oxide is slightly soluble in water. It can wash down the window with the rain. A thin, unobtrusive, and porous sorbent cartridge, such as activated carbon, can be placed at the bottom of the window in order to capture the mercury [38]. The capacity of the sorbent cartridge is such that it will last the lifetime of the cars and buildings. Proper disposal of the cartridge will prevent mercury from entering the food chain. Automobiles and buildings using these modified windows could constitute millions of passive mobile and stationary collectors of mercury from the air [38]. The concept is similar to that described by Hoke [42] for the use of metal catalyst stripes on automobile radiators for the destruction of air pollutants. Wang [43] described an attempt to alleviate air pollution in Asia by use of titania-coated building materials. Additionally, there are several common band-gap semiconductor oxides, including titanium dioxide, zinc oxide, tin oxide, and iron oxide, which can behave as photocatalysts for the oxidation of mercury [44]. These minerals are common constituents of the earth's crust and are present in the fine particulate matter present in air. These particles are released into the air by volcanoes, forest fires, dust storms, incineration of wastes, and combustion of fossil fuels. It is suggested that the interactions between mercury, long-wave ultraviolet radiation, and band-gap semiconductor oxides play an important role in the global cycling of mercury in the environment.

Experimental

The assembly used for studying the heterogeneous photocatalytic oxidation of mercury is a modified version of an apparatus described earlier [29]. It consists of an elemental mercury permeation tube within an air blending system, and various quartz or pyrex photoreactors with an ultraviolet lamp. Quartz or pyrex are used for the photoreactors because they are transparent to 365-nm light. An 8-in.-long, 6-W ultraviolet lamp from Spectroline (Spectronics BLE-6365S) is used as the source of the 365-nm light. The quartz tubes, pyrex reactors, and titania-coated glass plates are initially cleaned by rinsing first with trace-metals-grade 37% hydrochloric acid, then with distilled water, and last with reagent grade acetone. The permeation tube, located in a heated bath, is held at 212° F in a nitrogen stream at all times and releases 151 ng of elemental Hg/min.

A quartz photoreactor was employed for examination of the removal of mercury from oxygen-nitrogen-carbon dioxide-water vapor mixtures by a high surface area titanium dioxide powder. The fresh titanium dioxide powder contains 0.2 ppm of mercury, and has a BET surface area of 200 m²/gram. The photoreactor is a 1/4-inch-outer diameter tube described in an earlier paper. A 6 Watt ultraviolet lamp was used as the source of 365-nm radiation in all of the experiments. The intensity of the incident long-wave ultraviolet light upon the powder was 1.0 mW/cm². The gas compositions examined were oxygen-nitrogen-carbon dioxide mixtures similar to air. These compositions are:

A: 14% O₂, 270 ppb Hg, 240 ppm CO₂, 86% N₂
 B: 21% O₂, 270 ppb Hg, 360 ppm CO₂, 79% N₂
 C: 21% O₂, 270 ppb Hg, 360 ppm CO₂, 0-2% H₂O, 77-79% N₂

The gas flow-rate used was 60 ml/min. All experiments were conducted at ambient temperature and pressure.

Samples of the self-cleaning glass were obtained from a PPG-approved supplier. A small pyrex and large pyrex photoreactor were constructed for the glass samples. The small reactor was a 4-cm inner diameter by 25-cm pyrex vacuum trap from Southeastern Laboratory Apparatus. The trap was positioned horizontally over the ultraviolet lamp parallel to its major axis. Smaller irregular-shaped, cut plates were inserted into the reactor with the titania-coated surface face down. Gas was introduced through the center tube and vented from the trap inlet. To reduce bypassing, gas flow in later experiments was directed across the titania-coated glass by use of low density polyethylene bags wadded to produce a baffle and wedged behind the glass sample. Measured light intensities were between 1.2 and 1.8 mW/cm².

The large photoreactor was a 4000-ml pyrex kettle. Rectangular-shaped samples (15-cm by 10-cm) of the self-cleaning glass were inserted into the large reactor. The gas stream was introduced by a 0.3-cm outer diameter teflon tube located near the center of the glass samples. Light intensity at the plate surface was approximately 0.4 mW/cm².

Cold vapor atomic absorption spectrophotometry (CVAAS) was used to determine the mass of mercury contained on both the used titania powder (yellow in color) and titania-coated glass plates. Acidic solutions were employed to dissolve the mercury; the resulting solutions were analyzed by CVAAS. X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy with energy-dispersive X-ray methods (SEM-EDX) were utilized to confirm the formation of mercuric oxide on the titania surfaces.

Results

A high surface area titania powder was examined in the 1/4-inch photoreactor. The powder was exposed to Gas A for 350 minutes. A large percentage (44.2%) of the mercury was captured as yellow mercuric oxide (Table 4). Little mercury was captured in the absence of long-wave ultraviolet light. These results encouraged further tests with the self-cleaning glass plates. Table 5 shows the mercury levels present in the titania-coated glass blanks. The freshly cleaned glass plates have a very low concentration of mercury (below 0.0001 µg/cm²). Capture of mercury is not observed upon exposure of the titania-coated glass to Gas A in the absence of long-wave ultraviolet radiation.

The mercury removal by titania-coated glass exposed to Gas A and irradiated by 365-nm light is shown in Table 6. A variable level of mercury was captured by the glass. XPS analysis determined that mercury is present on the surface of the used plates as mercuric oxide. The removal varies with the exposure time and superficial glass surface area. The removals appear to be surface area

limited. The radiation intensity is comparable to mid-day summer incident sunlight in Pittsburgh.

Mercury capture by the glass plates exposed to Gases B and C and irradiated by 365-nm light is presented in Table 7. The presence of water vapor in Gas C appears to significantly enhance the capture of mercury.

There is scatter in the mercury removals obtained by irradiation of Gas C using the 25 cm² coated glass plate, as shown by the 33% standard deviation. Several factors impact the uncertainties in the mercury removals. The intensity of light diminishes with the square of the distance from the source. The uncertainty in the distance between the lamp and the photoreactor was $\pm 1/16$ in., introducing an uncertainty in the intensity of 15%. Additionally, an uncertainty in the mercury capture is introduced by the CVAAS analysis. The uncertainty associated with the recovery and CVAAS measurement of mercury is at least $\pm 10\%$. The mercury output from the permeation tube has an uncertainty level of at least $\pm 6\%$. Therefore, the scatter in the mercury removals is not surprising. Nevertheless, analyses with XPS and SEM-EDX showed that mercury in the oxygen-nitrogen mixtures is oxidized by the titania powder and coated glass, forming mercuric oxide.

Discussion

The screening results shown in Tables 6 and 7 suggest that titania-coated glass plates can sequester mercury from the air. It is noted that the concentration of elemental mercury (270 ppb) used in the experiments is five orders of magnitude greater than the concentration of elemental mercury typically found in ambient air (1 ppt). The extraordinarily small concentration of elemental mercury in air will result in fewer collisions between mercury atoms and the titania surface. This may result in less efficient capture of mercury by titania-coated glass in ambient air.

The addition of water vapor to the oxygen-nitrogen mixtures resulted in a greater level of mercury capture. This result was expected, as both gas phase oxygen and water vapor can serve as oxidants with a titania photocatalyst [44].

In addition, there are other oxidizable compounds present in air, such as methane, hydrogen, carbon monoxide, and sulfur dioxide, shown in Table 2 [45]. It is expected that a titania surface will catalyze the oxidation of these species, possibly in competition with the oxidation of elemental mercury. This may reduce the capture of elemental mercury from air by titania-coated glass plates.

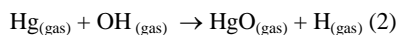
Heterogeneous photocatalytic oxidation can affect the fate of mercury in the atmosphere. Mercuric oxide, associated with fine particulates, has been detected recently in the tropopause [3,4]. Ambient concentrations of elemental mercury in the polar regions has been found to vary with seasonal changes in sunlight [5].

Table 3 lists several common band-gap semiconductors. The band-gap energies and corresponding maximum excitation wavelengths are tabulated [46]. The maximum excitation wavelengths are typically in the ultraviolet or visible light regions. Photons containing the band-gap energy can induce the formation of reactive radicals such as hydroxyl, as well as other reactive oxygen species, on the semiconductor surface [44]. Kaluza found

that elemental mercury can be photooxidized by titania, zinc oxide, tin oxide, and cerium oxide [44]. Kaluza also speculated that hydroxyl radicals (OH) and a chemisorbed charged oxygen species (O₂⁻) are responsible for the photooxidation of mercury on titania [44]. Alpha alumina, and silica were found to be inactive photocatalysts for the oxidation of elemental mercury [44].

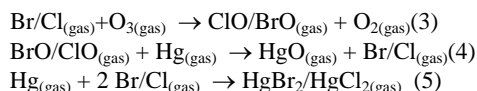
Various dopants have been previously examined to improve the efficiency of titania photocatalysts for the oxidation of hydrocarbon pollutants. Other band-gap semiconductor oxides have been studied for the oxidation of pollutants. These strategies could be employed in order to improve the capture of elemental mercury by coated glass, as well as to enhance the self-cleaning properties of the windows.

It is currently thought that elemental mercury is removed from the atmosphere by gas phase oxidation by ozone and hydroxyl radicals, viz [8]:



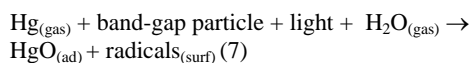
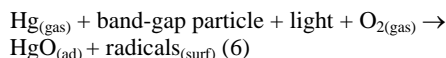
Reaction (1) is the gas phase oxidation of elemental mercury by ozone to form mercuric oxide. Reaction (2) is the gas phase oxidation of elemental mercury by hydroxyl radical to form mercuric oxide and a hydrogen radical. The gas-phase concentrations of elemental mercury, ozone, and hydroxyl, as well as the rate constants for reactions (1) and (2) are consistent with the long half life of elemental mercury in the atmosphere [8].

In the polar regions, halogen and halogen oxide radicals originating from sea spray are hypothesized to oxidize mercury, viz [10]:



Reaction (3) is the photochemical depletion of ozone by halogens. Reaction (4) is the gas phase oxidation of elemental mercury by halogen oxides to form mercuric oxide and halogen radicals. Reaction (5) is the oxidation of elemental mercury by halogen radicals to form gas phase mercuric chloride and mercuric bromide. This mechanism has been proposed by Lindberg in order to account for the depletion of ambient elemental mercury observed during springtime polar sunrise [10].

The heterogeneous photooxidation of elemental mercury by band-gap semiconductors is another potential route for the deposition of mercury. The overall reactions can be crudely represented by equations (6) and (7):



The surface radicals or charged oxygen entities can recombine to form oxygen or water, or react with other

oxidizable adsorbed species. Band-gap semiconductors which potentially could participate in reactions (6) and (7) include titanium oxide, zinc oxide, tin oxide, iron oxide, cerium oxide, and carbon. Xie found titanium and zinc present in Arctic aerosols [9]. The ubiquitous nature of these common fine band-gap semiconductor particulates suggests that they may play a role in the oxidation of elemental mercury in the atmosphere. Schroeder had earlier found mercuric oxide associated with fine particulates in the upper atmosphere of the Arctic [5].

The possibility that carbon fine particles can act as heterogeneous photocatalysts for the oxidation of elemental mercury requires further examination. The band-gap energy of carbon (Table 3) suggests that short wave ultraviolet radiation is required for it to behave as a photocatalyst for the oxidation of mercury. This could occur in the upper atmosphere, where short wave ultraviolet light is more prevalent than in the lower atmosphere.

Conclusions

Photo-oxidation of mercury with self-cleaning glass is a method for sequestration from ambient air. A preliminary estimate suggests that a substantial quantity of mercury could be removed from the atmosphere by wide-scale utilization of the self-cleaning glass-sorbent cartridge apparatus. Passive removal of mercury from air has several advantages over costly point source removal techniques and is a unique approach to the problem of mercury in the food chain. Capture of elemental mercury from oxygen-nitrogen mixtures has been demonstrated. The intensity of the incident long-wave ultraviolet radiation is comparable to sunlight. Passive removal of mercury should be reliable as no moving parts or external power supplies are necessary. The presence of moisture resulted in higher levels of mercury capture, possibly due to the formation of hydroxyl radicals on the glass surface. Future research should focus on mercury capture from more dilute mercury mixtures (at part per trillion by volume levels) representative of air. The effect of other oxidizable species present in air (such as methane, hydrogen, carbon monoxide, and sulfur dioxide) upon the removal of mercury needs to be determined. Other band-gap semiconductor oxide coatings should be studied for the capture of elemental mercury, as well as to enhance the self-cleaning properties of the windows.

Sunlight is a major factor in the transport and transformations of mercury in the environment. The interactions of mercury with band-gap semiconductor oxides may be a significant factor in the global mercury cycle. The ubiquitous nature of long-wave ultraviolet radiation and band-gap semiconductor oxide fine particles suggests that they drive the atmospheric transformations of mercury between the elemental, oxidized, and particulate-bound forms. Photo-oxidation by band-gap semiconductor oxide fine particles could be a factor in the seasonal fluctuations of elemental mercury in the atmosphere. Photocatalytic oxidation of elemental mercury by carbon particulates, if confirmed, would have major implications for the global cycle of mercury.

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Disclaimer

Reference to any specific commercial product or service is to facilitate understanding and does not imply endorsement by the United States Department of Energy.

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Table 1. Typical Untreated Flue Gas Composition From a Pulverized Coal Combustor Burning a Low-Sulfur Bituminous Coal [16, 29]

<u>Species</u>	<u>Concentration (by volume)</u>
H ₂ O	5-7%
O ₂	3-4%
CO ₂	15-16%
total Hg	1 ppb
CO	20 ppm
hydrocarbons	10 ppm
HCl	100 ppm
SO ₂	800 ppm
SO ₃	10 ppm
NO _x	500 ppm
N ₂	balance

Table 2. Typical Composition of Air (Dry-Basis) Near Sea Level [8, 45]

<u>Component</u>	<u>Concentration (by volume)</u>
N ₂	78.1 %
O ₂	20.9 %
Noble Gases	0.9 %
Total Hg	1 ppt
CO ₂	360 ppm
CH ₄	2 ppm
H ₂	0.5 ppm
CO	trace
SO ₂	trace
NO ₂	trace
others	balance

Table 3. Band-Gap Semiconductors Present in Air [46]

<u>Semiconductor</u>	<u>Band-Gap E_{gap} (eV)</u>	<u>Maximum Excitation Wavelength</u> $\lambda_{\text{max}} = hc/E_{\text{gap}}$ (nm)
TiO ₂	3.0	414 (long wave ultraviolet)
ZnO	3.2	388 (long wave ultraviolet)
Fe ₂ O ₃	2.0	620 (visible light)
SnO ₂	3.6	345 (long wave ultraviolet)
CeO ₂	3.2	388 (long wave ultraviolet)
Carbon	5.2	239 (short wave ultraviolet)

Table 4. Mercury Capture By Titania Powder

<u>Gas</u>	<u>Exposure (min)</u>	<u>Mercury Capture (%)</u>
A	350	44.2
A (No UV)	350	1.2

Table 5. Mercury Levels in Titania-Coated Glass Blanks

<u>Glass Area cm²</u>	<u>Exposure (min)</u>	<u>Loading $\mu\text{g Hg/cm}^2$</u>
155	0	less than 0.0001
16	0	less than 0.0001
155 (Gas A)	300 (no UV)	less than 0.0001

Table 6. Mercury Capture By Titania-Coated Glass Plates: Small Reactor, Gas A

<u>Glass Area cm²</u>	<u>Exposure (min)</u>	<u>Loading $\mu\text{g Hg/cm}^2$</u>	<u>% Mercury Capture</u>
16	350	0.2	5.9
155	360	0.03	8.9
33	745	0.37	10.1
16	990	0.16	1.8
139	990	0.48	42.4
5	1050	0.23	0.7
33	1369	0.22	3.2
4	2490	0.47	0.5

Table 7. Mercury Capture By Titania-Coated Glass Plates: Gases B&C

<u>Glass Area cm²</u>		<u>Exposure (min)</u>	<u>Loading $\mu\text{g Hg/cm}^2$</u>	<u>% Mercury Capture</u>
25	Gas B	990	0.03	0.5
25	Gas C	995	0.51	8.5
25	Gas C	3900	5.0	21.2
25	Gas C	4065	7.0	28.7
25	Gas C	3900	3.4	14.4

EVALUATIONS OF A NOVEL SAMPLE CONDITIONING SYSTEM FOR THE CONTINUOUS REAL-TIME MONITORING OF MERCURY IN FLUE GAS FROM COAL-FIRED UTILITY BOILERS

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Introduction

Mercury (Hg) from combustion sources is recognized as a major concern to the nations air quality. In December 2000, EPA announced that it would regulate mercury emissions from coal-fired boilers under Title III of the Clean Air Act Amendments of 1990. A key aspect of achieving and assuring compliance is the ability to accurately measure mercury at a regular interval. The optimal solution is a continuous emissions monitor for mercury that could be operated and maintained in a similar manner as already done with SO₂ and NO_x CEMs at utilities. Although a few mercury analyzers show promise for measuring elemental mercury, a reliable sampling system that will allow these analyzers to measure total (particulate plus vapor) and speciated mercury continuously in the flue gas of coal-fired utility boilers has not been demonstrated and recent development efforts are still in the early stages.

Real-time continuous monitoring of mercury in flue gas is essential for several reasons. Control of Hg emissions from coal-fired utility boilers is currently being considered, and if implemented will likely cost billions of dollars each year (i). Most of the Hg control strategies being proposed for coal-fired utility boiler flue gas include some type of sorbent injection. Prior to installing a control system, more accurate measurements of Hg emissions would allow EPA and the utility to make more informed decisions concerning their needs and control options. Real-time continuous monitoring of Hg would provide options for advanced process control feed-back as well as for monitoring the performance of the control system, thus minimizing sorbent usage and lowering the cost of controls. Other applications of this technology include Hg emission monitoring from other sources, such as municipal waste incinerators, commercial/industrial boilers, medical waste incinerators, and crematories.

In a effort to advance the art of mercury measurements, Apogee was awarded a Phase I and II Small Business Innovative Research Grant (SBIR) from EPA and additional funds from the Electric Power Research Institute (EPRI) to develop a prototype Sample Conditioning System (SCS) that, in conjunction with currently available analyzers (e.g., cold vapor atomic absorption spectrometers (CVAAS), cold vapor atomic fluorescence spectrometers (CVAAFS)), will enable real-time monitoring of total vapor-phase mercury (TVM), elemental mercury (EM), and oxidized mercury (OM) as well as total mercury (TM), consisting of particulate mercury (PM) and TVM.

The overall goal of this program is to define a new state-of-the-art mercury measurement system by developing a novel "front-end" conditioning system for the continuous real-time monitoring of mercury in flue gas from coal-fired utilities. The SCS will provide a method to use an analyzer such as CVAAS or CVAFS to measure TVM, EM, and TM.

Great River Energy (GRE), PSEG Fossil, LLC, WE Energies and Xcel Energy offered their support and one of their facilities as test sites. Field evaluations of the SCS were conducted at the three test locations to demonstrate the mercury SCS at plants firing low-chlorine North Dakota lignite, a high-chlorine low-sulfur eastern bituminous coal, and a Powered River Basin (PRB) coal. The

complete system was evaluated at the low-chlorine coal site (Site 1) using procedures described in the EPA PS-12. Testing included calibration zero and drift checks over a seven-day period, calibration error evaluations, and relative accuracy test using the Draft Ontario Hydro method as the reference method. Long-term evaluations at the high-chlorine coal site (Site 2) and the PRB site (Site 3) have been concluded. A month-long evaluation of the system is currently underway at a PRB site (Site 4). Data from this evaluation will be presented at the conference.

Experimental

Sample Conditioning System

There are around a dozen commercially available Hg CEMs and all have their pros and cons. The real challenging part of any system is the sample conditioning portion or also called the front-end. Challenges include: fly ash interactions with the Hg in the flue gas, adsorption and absorption, obtaining a TM concentration, which includes particulate phase, and obtaining a particulate free gas stream with minimal maintenance.

The SCS, as shown in Figure 1, will provide a method to use an analyzer such as a CVAAS, Zeeman, or CVAFS to measure TVM, EM and TM. The vapor-phase portion of the system is a dual pass design, where TVM passes through one line and the elemental fraction through the second line. Particulate is removed from a common sampling probe and the flow is split to the two lines. All components in the two lines are identical except that soluble OM is removed from the sample gas stream upstream of other components in the first line. In both lines, the gas stream then passes through a catalyst to convert mercury to the elemental form. The gas is then conditioned to remove possible interfering gases and stabilize the EM prior to transport to an analyzer for measurement. In the system, sample conditioning takes place at the stack and only EM is being conveyed from the stack to the analyzer. Thus, problems related to reactivity and surface losses are minimized. For TM, a slipstream of flue gas is isokinetically extracted and heated to thermally desorb mercury from the fly ash. The effluent is then filtered and passed through a second TVM SCS line for measurement.

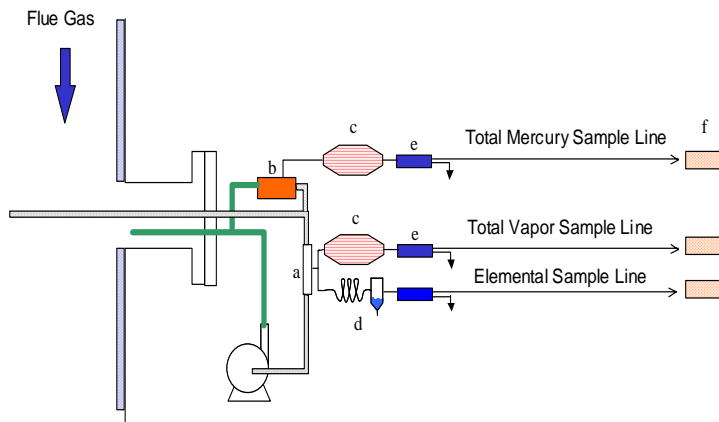


Figure 1. SCS arrangement for simultaneous measurement of TM, TVM, and EM.

Evaluation Methods

During field evaluations at the low-chlorine coal site, the performance specification test procedure identified in EPA's Draft

Performance Specification (PS-12) (see Table 1) was followed.

Apogee utilized two techniques to calibrate the mercury analyzer during SCS operation. The primary technique was the batch injection method. For this technique, a precise volume of mercury vapor is drawn off a flask containing liquid elemental mercury using a glass/TeflonTM syringe. A temperature and pressure measurement was taken before each sample drawn. When continuous concentrations of mercury are required, Apogee uses an elemental mercury permeation tube. If tests are conducted at a field site where the environmental conditions vary significantly, the mercury emitted from the permeation tube is referenced to the spike calibration technique. When a continuous concentration of OM was required for calibration, gas from the EM permeation tube was passed through a catalyst that converted 100% of the EM to OM. This technique simplifies calibration because the concentration of total mercury measured by the analyzer should remain unchanged regardless of the presence of the EM to OM conversion catalyst. During the zero drift evaluation, no mercury was injected into the analyzer. A sample collection time of zero was set prior to evaluation. After the zero drift evaluation, a calculated amount of mercury vapor (approximately 50% of the duct concentration) was injected. Both the known concentration and the analyzer concentration were recorded. Other analyzer parameters were recorded as well to further evaluate analyzer performance. A second calibration concentration (approximately 100% of the duct concentration) was injected into the purge dry-gas line of the analyzer.

To confirm the measurements obtained with the SCS while on-site, a standard impinger based method was initially used. A reduction solution of stannous chloride in hydrochloric acid was used to convert OM to EM. The solution is mixed as prescribed in the draft Ontario Hydro Method for Manual Mercury Measurements. To measure speciated mercury, an impinger of potassium chloride (KCl) solution mixed as prescribed by the draft Ontario Hydro Method was used to capture oxidized mercury. Impinger solutions are continuously refreshed to assure continuous exposure of the gas to active chemicals.

Results and Discussion

Site 1 (Low-Chlorine Coal)

Apogee has completed field evaluations at one coal-fired utility that burns North Dakota Lignite coal, a low chlorine coal that produces a flue gas with primarily elemental mercury. The unit has two cold-side ESPs operating in parallel followed by a single scrubber. The test location was downstream of the ESP and upstream of the scrubber for a dry, low chlorine sample. The system was subjected to the EPA draft PS-12 and performed very well. Results from this site have been presented previously at numerous conferences.

Site 2 (High-Chlorine Coal)

Apogee has completed field evaluations at a coal-fired utility that burns a bituminous fuel; a high chlorine coal that produces a flue gas with primarily oxidized forms of mercury. The unit has two cold-side ESPs operating in parallel. The test location was downstream of the ESPs. The oxidized removal module performed very well at the site, however the total vapor mercury (TVM) module initially encountered some difficulties with the flue gas chemistry. The TVM module's initial performance was characterized by an initially stable mercury concentration that would begin to decay over time until finally no mercury was being transported to the analyzer at all. After investigation it was determined that vapor-phase selenium was being reduced to hydrogen selenide, which was reacting with the elemental mercury at the exit of the module. A gas stream additive was found which eliminated the problem. Evaluations were performed to verify

the performance of the system with the selenium mitigation. The results were very good, despite the fact that the mitigation method had not been optimized. The TVM module was operated with an overboard calibration system to verify its performance. Data will be presented at the conference showing the performance of the TVM and also a discussion of the selenium-mitigation modification.

Site 3 (PRB)

A long-term evaluation of the TVM module has been concluded at a PRB utility at a test location downstream of a wet-venturi scrubber. This evaluation compares the performance of the TVM module with the standard wet chemical method. The performance of the system was very good and results agreed with those seen in the wet-chemical system very well. Data will be presented at the conference concerning this evaluation.

Site 4 (PRB)

A month-long evaluation of the TVM module is currently underway at an additional PRB fuel site. The test location is downstream of a cold-side ESP. No data is currently available; data from this evaluation will be presented at the conference.

Conclusions

It is possible to measure mercury in the flue gas from coal-fired boilers using mercury analyzers and current "wet chemistry" technologies, however these techniques require significant care and attention by highly skilled personnel to achieve reasonable results. As of yet, this is not currently an option for meeting the emissions measurement needs beyond research applications. Several groups, including Apogee, are developing techniques to advance the way mercury measurements are taken. These techniques will require more field evaluations to assure that they are reliable in the majority of flue gas streams and able to be utilized over long periods.

Acknowledgements

Apogee would like to acknowledge the funding of EPA through an SBIR grant (Contract 68-D-01-060) and Project Manager James Gallup, EPRI's generous support and Project Manager Chuck Dene, and the support of Great River Energy, PSEG Fossil, and Xcel Energy.

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Characters of Activated Carbon for Hg Removal of Flue Gas with H₂S and Iron Oxide for Hg Removal of Coal Derived Fuel gas with H₂S

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Introduction

The major anthropogenic sources of mercury emission are coal combustion and municipal waste incineration. However, it is very difficult to remove the mercury compounds, particularly elemental mercury vapor, which is not effectively captured in typical air – pollution control devices. It has been reported that activated carbon, particularly activated carbon impregnated with sulfur, chlorine, and iodine, are effective for Hg removal.¹⁻⁴⁾ However, the major drawbacks of activated carbons are high cost, poor capacity, narrow temperature range and slow regeneration and adsorption rates.

We have presented a novel Hg removal method using H₂S and adsorbents.^{5,6)} This method based on the reaction of H₂S and Hg over adsorbents. Although the reaction mechanism is not well understood yet, but it has been suggested in our previous report that Hg reacts with H₂S and forms HgS.⁵⁾ The sublimation point of HgS(cubic) is 446°C. If the reaction (adsorption) between Hg and H₂S over suitable adsorbent (catalyst) occurs at a temperature well below the sublimation point of HgS, then elemental mercury can be removed from the flue gas effectively. In this study, we tried to clarify the removal characters of an activated carbon and an iron oxide for the removal of Hg vapor: The activated carbon was useful for the Hg removal from a combustion flue gas; the iron oxide was useful for the Hg removal from a coal derived fuel gas.

Experimental

Sorbents. Activated Carbon (AC) was purchased from Wako Pure Chemical Co. LTD. The raw material of this activated carbon was coconut shell. The granular active carbon was washed with de-ionized water and calcined for 3h at 300° in the N₂ flow. The granular AC particles were sieved into an average diameter of 1.0mm. BET surface area measured using liquid nitrogen was ca. 1100m²/g. An iron oxide sample was prepared by a precipitation method using a reagent grade Fe(NO₃)₃·9H₂O and NH₃aq at room temperature. The precipitant was washed with de-ionized water and dried for 25h at 110°C under atmosphere. The dried sample contained FeO(OH). BET surface of the sample was ca.200m²/g.

Apparatus and Procedure. The evaluation of the reactivity of the samples was carried out using a flow-type packed bed reactor under atmospheric pressure. About 0.5 cm³ or 0.25 cm³ of the sample particles (diameter: 1.0mm) was set in quartz tube reactor. The reaction temperatures range examined was from 80 to 100°C. The reaction for Hg removal of flue gas was carried out with a mixture of Hg (4.8ppb), H₂S (0 or 40ppm), SO₂(0 or 250ppm), CO₂ (13%), H₂O(8%), O₂(5%), and N₂ (balance gas) at 500cm³STP/min (SV:6.0X10⁴ h⁻¹). The reaction for Hg removal of coal derived fuel gas commenced when a mixture of Hg(4.8ppb), H₂S(400ppm),

CO(30%), H₂(20%), H₂O(8%), and N₂ (balance gas) was fed into the reactor at 500 cm³STP/min (SV:12X10⁴ h⁻¹). The measurement of the inlet and outlet concentration of mercury were carried out using a cold vapor mercury analyzer.

Results and Discussion

Character of AC for removal of the flue gas with H₂S.

Effect of the temperature on the Hg removal in the both presence of H₂S and SO₂. As shown in Figure 1, there was a suitable temperature: the

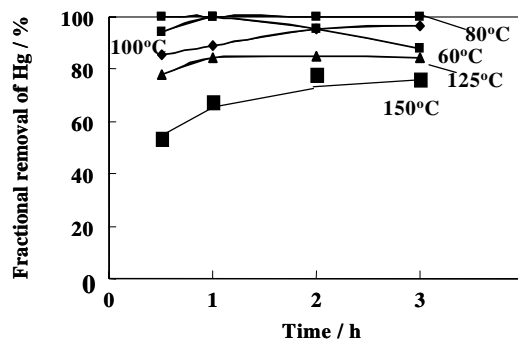


Figure 1. Effect of temperature on the Hg removal.

temperature range was 80 °C. The reason of this dependency of the temperature on reactivity may be explained by the removal mechanism if the mechanism is clarified.

Effect of the presence of SO₂ and H₂S on the Hg removal

The AC removed a negligible amount of Hg at 150°C in the presence of SO₂ or H₂S. However, in the both presence of SO₂ and H₂S, the AC could remove the considerable amount of the Hg as shown in Figure 1. This result may suggest that Claus reaction occurred over the AC and the produced sulfur reacted with the Hg vapor.

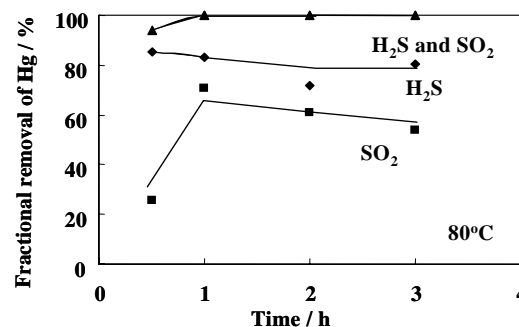
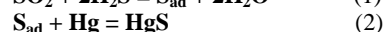
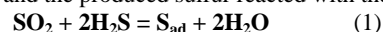


Figure 2 Effect of the presence of SO₂, H₂S and SO₂-H₂S.

As shown in Figure 2, the AC could remove a considerable amount of the Hg vapor in the only presence of SO₂ or H₂O at low temperature (80°C). In the both presence of SO₂ and H₂S, the AC could almost perfectly remove the Hg vapor as shown in Figure 1. This result suggests that the mechanism of the Hg removal with AC is different at the low- and the high-temperature. Furthermore, the difference of the mechanism in the temperature range may be a cause of the existence of the suitable temperature for the Hg removal.

Effect of the presence of H₂O on the Hg removal

The presence of H₂O at 100 and 80°C accelerated the Hg removal

with the AC in the both presence of H_2S and SO_2 . However, the presence of H_2O at $150^\circ C$ depressed the Hg removal with the AC as shown in **Figure 3**. This result also suggests that the mechanism of the Hg removal is different at the low and high temperature.

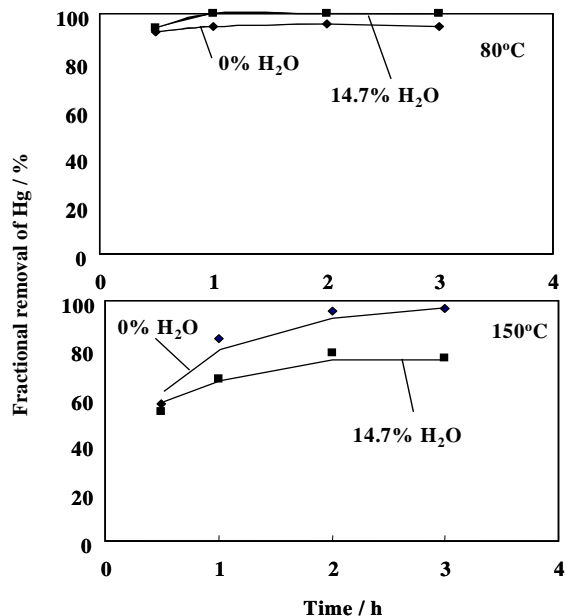


Figure 3. Effect of the presence of H_2O .

Character of the Iron oxide for Hg removal of the coal derived fuel gas with H_2S .

Effect of the temperature on the Hg removal

As shown in **Figure 4**, the activity of the iron oxide for the Hg removal increased with the decrease of the reaction temperature. After use of the iron oxide under the low temperature 60 and $80^\circ C$, the sample was not changed when it was exposed to the air. However, at the high temperature $150^\circ C$, the temperature of the used sample

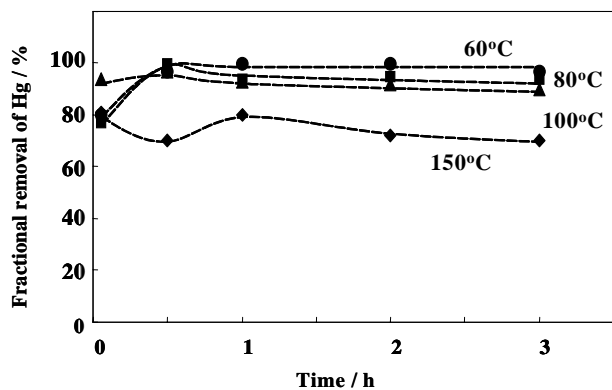


Figure 4. Effect of temperature on the Hg removal.

was increase when the used sample was exposed to the air. Furthermore, the sulfur smelled up from the sample at that time. After cooling in nitrogen atmosphere, another used sample was measured with XRD. We confirmed the formation of magnetite in the sample. From these results, it was suggested that the formed sulfur over the sample vaporized by heating when the sample magnetite

exothermally changed to hematite with air. Form these experimental results and consideration, it was supposed that sulfur formed from H_2S over the iron oxide contributed to the Hg removal and also the surface oxygen or part of the lattice oxygen of the sample iron oxide contribute to produce of sulfur from H_2S .

Effect of the presence of CO and H_2O on the Hg removal

As shown in **Figure 5**, the presence of CO at $150^\circ C$ accelerated the Hg removal but the acceleration of the presence of it at $80^\circ C$ was not observed. The effect of the presence of H_2 at $80^\circ C$ also did not observed

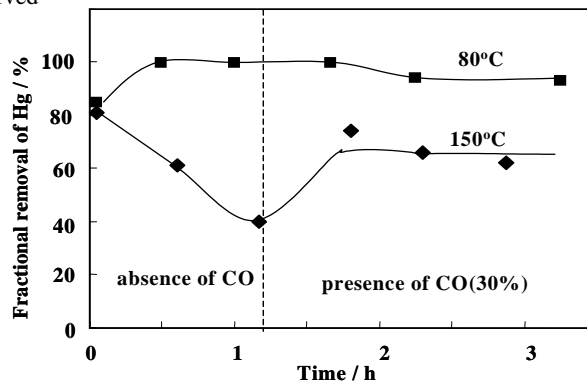


Figure 5. Effect of the presence of CO on the Hg removal

The presence of H_2O depressed the Hg removal in the temperature hole range from 60 to $150^\circ C$.

Conclusion

The characters of the Hg removal for the flue gas with the AC and the Hg removal for the fuel gas with the iron oxide could be considerably clarified.

Acknowledgment

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